EXECUTIVE SUMMARY

Integrating Atmospheric Mercury Deposition with Aquatic Cycling in South Florida:

An approach for conducting a Total Maximum Daily Load analysis for an atmospherically derived pollutant

Florida Department of Environmental Protection
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Purpose:

The purpose of this project was to demonstrate the technical feasibility of conducting a Total Maximum Daily Load (TMDL) analysis for a system where the contaminant of interest is derived principally from atmospheric sources. Depending on the type of aquatic system, a number of contaminants may be categorized as significantly atmospheric in origin, including mercury, fixed nitrogen, PCB's, and others. This study focuses on mercury, and incorporates extensive field data into a framework combining atmospheric mercury deposition and aquatic mercury cycling models to demonstrate the feasibility of the approach. The goal was to understand and simulate how changes in local atmospheric mercury emissions in south Florida would influence mercury concentrations in top predator fish, thus demonstrating the potential of combining air and water modeling approaches in TMDLs involving air deposition of mercury.

About 2 million acres of the south Florida Everglades ecosystem are currently under fish consumption advisories because of mercury contamination. The Clean Water Act requires that states list as impaired all waterbodies that do not meet water quality standards when the designated uses are not being met or because water quality criteria are being exceeded. Mercury-contamination fish consumption advisories represent an exceedance of water quality standards because a designated use for the Florida Everglades ecosystem is not being met. Once a waterbody such as the Everglades is placed on the Clean Water Act 303(d) list, a TMDL study is conducted to determine how much the pollutant (i.e., mercury) loading must be reduced, and from what sources, to meet the water quality standards and designated use for the waterbody. A TMDL establishes the maximum amount of a given pollutant that a particular waterbody can assimilate without exceeding surface water quality standards. TMDL-type analyses for determining needed reductions in atmospherically derived pollutants have rarely been done due to the data needs and technical complexity of developing and linking atmospheric and aquatic cycling models.

Mercury is both a naturally occurring element and a pollutant that cycles, in a variety of chemical forms, through air, water and soil. Some forms of mercury are transported around the world through the air, others tend to deposit from the atmosphere at local or regional scales. Extensive monitoring of the Florida Everglades ecosystem has shown that the primary source of mercury loading is atmospheric deposition – over 95% of the mercury load to the Everglades each year comes from atmospheric deposition. Because some atmospheric mercury is transported into Florida from both local and distant sources, a difficulty in producing a TMDL is determining the relative contribution of these sources. To conduct a TMDL analysis for mercury, atmospheric models are needed to simulate the transport of local mercury emissions and deposition onto the Everglades water surface. In addition, once the mercury deposition is estimated using atmospheric models, this deposition must be used as input to an aquatic ecosystem model that will simulate mercury cycling in the Everglades and uptake through the food chain to top predator fish, such as largemouth bass.

To that end, this modeling project was sponsored by the Florida Department of Environmental Protection and US Environmental Protection Agency to combine atmospheric mercury deposition models with an aquatic mercury cycling model. The mercury deposition output from the atmospheric models was used as input to an aquatic mercury cycling model. The aquatic mercury cycling model was used to predict the change in largemouth bass mercury concentrations that might occur if mercury emissions were reduced. The goal is to provide data and models that can be used to conduct a Total Maximum Daily Load study for mercury in the Everglades. [1]

Results and Conclusions

The following results were obtained from using output of the atmospheric model as input to the aquatic ecosystem model:

1. The E-MCM model predicts a linear relationship between atmospheric mercury deposition and mercury concentrations in largemouth bass, with a small residual mercury concentration in fish at zero atmospheric mercury deposition (Figure 9). In other words, for any reduction in mercury inputs to the Everglades a slightly lesser

[1] For additional information about the Florida DEP Mercury Program, access the web address given below: http://www.floridadep.org/labs/mercury/index.htm

reduction in fish mercury concentrations may be anticipated. Furthermore, error analysis shows that the E-MCM predicts near equivalence between the percent decrease in atmospheric mercury deposition rate and the percent decrease in largemouth bass mercury concentration over the likely range for current estimates of atmospheric deposition of mercury. The slight offset from a 1:1 relationship results from slow mobilization of historically deposited mercury from deeper sediment layers to the water column. Until buried below the active zone, this mercury can continue to cycle through the system. In addition, because mercury is a naturally occurring element, fish tissue mercury concentrations can never be reduced to zero.

2. In the absence of changes to the system other than mercury loading (e.g. changes in sulfur cycling, nutrient cycling, or hydrology), a reduction of about 80% of current total annual mercury atmospheric deposition rates would be needed for the mercury concentrations in a 3-year old largemouth bass at WCA 3A-15 to be reduced to less than Florida's present fish consumption advisory action level of 0.5 mg/kg (parts per million).
3. Mercury concentrations in three-year-old largemouth bass are predicted to achieve 50% of their long-term, steady state response following sustained mercury load reductions within approximately 10 years and 90% within 30 years (Figure 10).
4. Despite the uncertainties identified, the progress represented in these demonstrations of a unique combination of atmospheric and aquatic cycling models is remarkable. There is every reason to believe that, with modest additional effort, the remaining uncertainties can be reduced to levels that will allow reliable, confident allocation of mercury emissions to protect the designated uses of the Everglades.
5. It is also evident that there is further potential for combining such air and water modeling approaches for TMDLs involving air deposition of mercury for other aquatic ecosystems. We believe the approaches presented here can be applied to other geographic areas and in other studies of air – water chemical interactions.

Combining Atmospheric and Aquatic Models

The atmospheric modeling approach used in this study was developed by the University of Michigan Air Quality Laboratory to simulate the atmospheric transport of mercury from local emission point sources in southern Florida to its deposition onto the Everglades. The aquatic model, the Everglades Mercury Cycling Model (E-MCM), was used to simulate how mercury was cycled in the Everglades and accumulated through the Everglades food chain to top-level predator fish (e.g., largemouth bass, a popular sport fish).

The Florida Everglades ecosystem extends over 3,000 square miles, thus it was not realistic to simulate the entire ecosystem. However, extensive monitoring studies in the Everglades by USEPA (1998) revealed a mercury "hot spot" in central Water Conservation Area 3. The US Geological Survey subsequently conducted several years of intensive field study at this 'hot spot' (WCA 3A-15). Data from this site were used to calibrate the E-MCM model. Deposition and aquatic cycling data were available for 1995-1996; as a result, this period (22

June 1995 to 21 June 1996) was selected as the period of study. Atmospheric deposition rate for 1995-1996 is referred to as “current” deposition rate in this report.

Because of limited information and tools available to support modeling of a global transport domain, source-receptor modeling relied primarily on local sources to estimate deposition to the Everglades. As discussed in detail in Section 5.4.5 of the report, several lines of evidence suggest that local sources were the predominant contributor to mercury deposition on south Florida.

We acknowledge the global-scale cycling of some forms of mercury, but paucity of data or models to quantify or simulate this potential source to Florida puts this phenomenon beyond the reach of this analysis. An analysis by the principals of the FAMS project, independent of this work, examined rainfall mercury deposition in relation to trace element signatures of common sources of air pollution. They concluded that most mercury deposited at long-term south Florida deposition collection sites did not originate from local sources. Further field measurements and modeling analyses are underway to resolve this seeming paradox.

To estimate the deposition load to WCA 3A-15 measured wet deposition at multiple FAMS sites was combined with modeled dry deposition in this analysis. Estimating total deposition to the TMDL study site required analysis of historical weather patterns in south Florida and selecting representative wind direction and rainfall patterns to use in estimating both wet and dry mercury deposition over the area based on local point source mercury emissions. The atmospheric model was calibrated to 1995-96 mercury deposition rates (both dry and wet deposition). Different mercury deposition reduction scenarios were simulated (75, 50, 30, and 15% of current levels) and provided as input to the aquatic mercury cycling model.

The aquatic mercury cycling model was run using the projected estimates of mercury deposition onto the marsh water surface at WCA 3A-15. The E-MCM model was run for 200 years so that steady-state conditions would be reached between atmospheric mercury deposition and largemouth bass mercury concentrations at current deposition rates. A relationship between atmospheric mercury deposition and largemouth bass mercury concentration was developed using the results from each of the different mercury emission/deposition scenarios. In addition, the time required for largemouth bass mercury concentrations to decrease to 50% and 90% of their long term, steady state mercury concentrations based on the reduced mercury deposition scenarios was estimated to be 10 and 30 years, respectively.

Assumptions and Cautions

This analysis demonstrates that atmospheric and aquatic mercury cycling models can be combined and used to estimate the reduction in fish mercury concentration associated with reduced mercury deposition. However, several assumptions and cautions must be considered when interpreting these results:

1. This report is <u>not</u> a fully formed mercury TMDL intended for implementation; that was <u>not</u> the goal of the present analysis. However, this report does demonstrate the technical feasibility of a combined modeling analysis to encompass the multi-media aspects of an air-water-biota pollutant problem. It establishes a method that furthers the goal of conducting a mercury TMDL study for the Florida Everglades.
2. The contribution of global mercury emissions to current atmospheric mercury deposition in southern Florida is poorly understood. After model testing and evaluation to assess the strengths of the assumption, the final model analysis of the relationship between mercury emissions and atmospheric deposition assumed that most of the mercury in deposition was from local sources. Although the comparison between observed and predicted wet deposition rates based on this assumption was good, this remains an area of scientific debate.
3. The processes affecting the transformation of mercury in the atmosphere were poorly understood or quantified at the time of this report. Therefore, the atmospheric modeling may not accurately reflect the properties of the actual mercury species that are being deposited onto the Everglades.
4. Not all the aquatic cycling processes affecting the transformation of inorganic mercury to methylmercury (which is the toxic mercury species that accumulates in fish) are represented in detail in the Everglades Mercury Cycling Model. For example, sulfate reduction is an important to the process of transforming inorganic to methylmercury. Some of the byproducts of sulfate reduction bind inorganic and methylmercury, making them less available for biological uptake. The details of these processes are not yet understood, thus cannot be modeled. Until the model is progressively refined and parameterized these limitations might affect the results reported here.
5. Although the measurement set is drawn from extensive, quantitative research, uncertainties remain in all field measurements, but this uncertainty is not included in the modeled output. The magnitude of the uncertainty is unknown, but it can affect the interpretation and conclusions drawn from the results.
6. Natural year-to-year variation in mercury deposition can be relatively large. This natural variability has not been included in the minimum loading calculations (although the effects of this variability were examined over long time-frames through Monte Carlo analysis). The 1995-1996 period was used as the basis for this analysis because it is the 12 month period for which extensive field monitoring and modeling data were available. It was not, however, a typical year as 1995 and 1996 were relatively wet years in southern Florida.
7. Only one area of the Everglades was considered in the simulation - WCA 3A-15. Other areas in the Everglades might not respond similarly because of different habitat, food web dynamics and water quality.

Recommendations

The following actions are recommended in order to allow a formal TMDL to be conducted for the Florida Everglades:

1. Obtain better estimates of local vs. regional and global mercury contributions to south Florida. This is critical because estimates of regional plus global sources by various workers range from ca. 25 to >60% of the mercury deposition over southern Florida.

2. Incorporate the aquatic chemistry and cycling of sulfur into the Everglades Mercury Cycling Model. Sulfate is an important influence on the production of methylmercury, affecting not only mercury transformations, but also the biological availability of mercury for uptake. There is a strong sulfate gradient decreasing from north to south in the Everglades Protection Area that is an important cofactor controlling the severity of the mercury problem at any given site.

3. Apply the atmospheric and aquatic models to other areas of the Florida Everglades to see if similar changes occur in largemouth bass mercury concentrations following reduced atmospheric deposition of mercury.

4. Improve mercury emissions inventories and better describe mercury species' transformations in the atmosphere. These are critical information needs to improve mercury transport and fate modeling.

5. Obtain better estimates of the uncertainty in the study. Uncertainty can affect the interpretation and conclusions drawn. Uncertainties that potentially affect decisions regarding controlling local mercury emission sources should receive highest priority.

Cover, counterclockwise from top left:

Figure 1. Florida Fish and Wildlife Conservation Commission biologists collecting early fish samples for heavy metals analysis from the Chipola River. Courtesy Andrew Reich, Fla. Dept. Health. 1984.

Figure 2. Florida Atmospheric Mercury Study sampling tower at the Everglades Nutrient Removal Project. Courtesy SFWMD.

Figure 3. Thunderstorm over the central Florida Everglades. Courtesy Dan Scheidt, USEPA Region 4.

Figure 4. Experimental mesocosms for elucidating mercury biogeochemistry in the Florida Everglades. Courtesy C. Gilmour, Academy of Natural Sciences and D. Krabbenhoft, USGS. ACME Project.

Figure 5. USEPA Region 4 REMAP graphic showing spatial distribution of mercury in mosquitofish across the Everglades Protection Area, with overlay of mercury in great egret chicks from active colonies. Spatial information on fish mercury courtesy EPA Region 4, SESD; wading bird data courtesy P. Frederick, University of Florida.

Figure 6. Wood storks feeding in the Florida Everglades. Courtesy SFWMD.

This project and the preparation of this report was funded in part by a Section 103 Air Pollution Control Grant from the U.S. Environmental Protection Agency (US EPA) through a contract with the Mercury and Environmental Science Program of the Florida Department of Environmental Protection. The total cost of the project was $ 543,351 of which $161,880 or 28 percent was provided by USEPA.

South Florida Mercury Science Program

FOREWORD

This document presents the results of a pilot project designed to evaluate the technical feasibility, given the present state of knowledge of mercury cycling in the environment, of calculating an atmospherically driven total maximum daily load (TMDL) for mercury for the Florida Everglades. This is among the first efforts to integrate atmospheric and aquatic cycling of a pollutant in a combined modeling analysis, as would be required for use in pollutant TMDLs where an atmospheric sources may be important contributors to pollutant loads. This project is not being conducted by Florida DEP with the expectation that it will be used as the basis for implementing changes to source permits or other action. Its purpose is to provide a technical analysis to provide the basis for a more comprehensive approach to a full TMDL process to be conducted subsequently.

This analysis is built upon extensive results from research on the sources, transport and fate of mercury in south Florida, and focuses on modeling approaches that might be used in the context of a TMDL for mercury deposited from the atmosphere. Florida law specifies the process the state will use for developing TMDLs for implementation. This law directs development of rules for the method of designating impaired waters and for the TMDL analysis itself. Any future TMDL analysis intended to be used to support policy will have to conform to these legal strictures. The Rule has been adopted but is subject to further review by the USEPA. As agreed between Florida DEP and USEPA Region 4, the schedule for TMDL implementation does not require completion of atmospheric TMDLs for mercury until 2010. The purpose of this project is to establish the technical basis for more definitive efforts in the future. This project is a collaborative, voluntary effort between DEP and USEPA.

This analysis was conducted for a portion of the Everglades known as Water Conservation Area 3A. This area was chosen because it offered a wealth of information gained from the extensive monitoring, modeling and research conducted by the cooperating agencies of the South Florida Mercury Science Program. This fruitful collaboration among state, federal and private groups has greatly illuminated the causes of the mercury problem in the Everglades, and by extension, the causes of the problem that exists across much of our country.

This and a similar effort being conducted by the Wisconsin Department of Natural Resources, represent an early effort to examine the issues that arise when a TMDL addresses atmospheric sources. As originally set forth in the Clean Water Act 30 years ago, TMDL analyses were conceived for direct discharge of wastes to a waterbody to address simple water quality problems such as low dissolved oxygen caused by excessive biological oxygen demand. However, it has since become apparent that pollutants from the atmosphere can represent significant loads to water bodies. Pioneering studies in Chesapeake Bay and the Great Lakes have demonstrated that the atmosphere can be a large source of nutrients or toxic substances to water bodies. Similarly, for the Florida Everglades, average annual atmospheric deposition rates for mercury outweigh surface water input by more than 20:1 (USEPA, 1998).

While the concept of an atmospheric TMDL may seem straightforward, the technical challenges in coupling air source pollutant emissions, chemistry and transport with the complex aquatic cycling and fate of mercury are daunting. At this time, significant uncertainties remain in our basic understanding of the atmospheric mercury cycle and modeling of mercury transport and fate, and likewise in our understanding of the aquatic cycling transformation processes and mercury bioaccumulation in aquatic food webs.

We wish to thank our many collaborators of the South Florida Mercury Science Program for their data, analyses, guidance, advice and efforts in the preparation of this document. We especially wish to thank William J. Bigler (DOH, retired), Forrest Ware (FWC, retired) and Thomas Savage (DEP, retired) who began the monitoring that led to the discovery of the mercury problem in Florida and which ultimately provided impetus for this work.

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ACME	Aquatic Cycling of Mercury in the Everglades study, USGS
AT	Andytown monitoring site of the Florida Atmospheric Mercury Study (FAMS)
CMAQ	Community Multiscale Air Quality Model, an USEPA/NOAA atmospheric chemistry, transport and deposition model
CWA	Clean Water Act
DEP	Florida Department of Environmental Protection
DOH	Florida Department of Health
EAA	Everglades Agricultural Area
ENP	Everglades National Park
EPA	Everglades Protection Area (i.e. Water Conservation Areas and the Everglades National Park)
E-MCM	Everglades Mercury Cycling Model
FAMS	Florida Atmospheric Mercury Study
FEDDS	Florida Everglades Dry Deposition Study
FS	Fakahatchee Strand State Park monitoring site of the Florida Atmospheric Mercury Study (FAMS)
FWC	Florida Fish and Wildlife Conservation Commission
GIS	Geographic Information System, computer mapping system
GMT	Greenwich Mean Time (5 hours earlier than USA east coast time)
Hg	The chemical notation for the element mercury, derived from the Greek Hydrargyrum
Hg(0)	Elemental mercury, the silvery metal liquid at room temperature
Hg(II)	divalent mercury, a form of inorganic mercury; mercuric ion, RGM
Hg(p)	Atmospheric particulate-associated mercury
Hg_t, Hg_{tot}	Total mercury, i.e. lab analysis of all forms of mercury
HYSPLIT_4	Hybrid Single Particle Lagrangian Integrated Trajectories Model, a NOAA atmospheric transport & deposition model
LMB	Largemouth bass
mb	millibars of pressure in the atmosphere
MCM	Mercury Cycling Model
MDN	Mercury Deposition Network, a sub-network of the National Atmospheric Deposition Program
mg/kg	milligrams per kilogram, a unit of measure of concentration, ppm
MeHg	Methylmercury
METAALICUS	Mercury Experiment To Assess Atmospheric Loading in Canada and the United States
MSRTC	Mercury Study Report to Congress (USEPA 1997)

MWC	Municipal Waste Combustors, (aka., Municipal Solid Waste Incinerator)
MWI	Medical Waste Incineration
NADP	National Atmospheric Deposition Program
ng/L	nanograms per liter, unit of measure of concentration, ppt
NCEP	NOAA National Center for Environmental Prediction
NGM	Nested Grid Model
NOAA – ARL	National Oceanic and Atmospheric Administration – Air Resources Lab
NPDES	National Pollutant Discharge Elimination System
ppb	parts per billion, a unit of measure of concentration,
ppm	parts per million, a unit of measure of concentration
ppt	parts per trillion, a unit of measure of concentration
RAMS	Regional Atmospheric Modeling System
RELMAP	Regional Lagrangian Model of Air Pollution
REMAP	Regional – Environmental Monitoring Assessment Program
RGM	Reactive Gaseous Mercury
SFMSP	South Florida Mercury Science Program
SFWMD	South Florida Water Management District
SoFAMMS	South Florida Atmospheric Mercury Monitoring Pilot Study
TGM	Total Gaseous Mercury
TMDL	Total Maximum Daily Load
TT	Tamiami Trail monitoring site of the Florida Atmospheric Mercury Study (FAMS)
UMAQL	University of Michigan Air Quality Laboratory
USEPA	U.S. Environmental Protection Agency
USFWS	U.S. Fish and Wildlife Service
USGS	U.S. Geological Survey
μg/L	micrograms per liter, a unit of measure of concentration, ppb
μeq/L	microequivalents per liter, a unit of measure of concentration
WCA	Water Conservation Area, a subdivision of the Everglades

1 BACKGROUND

Our understanding of the biogeochemical cycle of mercury has improved dramatically within the past decade. Prior to the development of ‘clean’ sampling and ‘ultra-trace’ analytical procedures, concentrations or pools of mercury in air, rain and surface waters, and the fluxes between these compartments, were commonly overestimated, in some cases by two to three orders of magnitude (Fitzgerald, 1986, 1989). Against this inflated backdrop, anthropogenic sources of mercury to the atmosphere of all types appeared small, with estimates of natural emissions accounting for 90 to 95 percent of total cycle. By the early 1990’s, application of more accurate measurements of the global pools and fluxes of mercury overturned this view, leading to the conclusion that natural emissions were “*between 20 and 50 percent of the direct and indirect anthropogenic sources*” (Expert Panel, 1994). Present estimates tend toward the lower end of this range. This new insight into the ‘natural vs. anthropogenic’ question, plus the finding that the accumulation of mercury in seepage lakes in remote areas is largely attributable to atmospheric inputs (Watras, *et al.,* 1994), has changed the way the mercury problem is viewed. Attention now focuses beyond the problem of elevated mercury in fishes in these lakes to the importance of deposition processes, atmospheric transport and chemistry, and ultimately to sources of mercury to the atmosphere.

The view that anthropogenic sources of mercury to the atmosphere predominate is buttressed by studies of long-term trends of mercury in the environment by examination of cores of sediments and similar media. “*Considered individually, these methods are subject to much uncertainty. However, when considered as a whole they indicate that the total atmospheric mercury burden has increased since the beginning of the industrialized period by between a factor of two and five*.” (Expert Panel, 1994). The significance of this increase is confounded by lack of uniformity, both temporally and geographically. For example, in some areas it has been shown that mercury deposition peaked between 1950 and 1970, at a level about three times present deposition rates. (Engstrom and Swain, 1997; Zillioux, *et al.*, 1993). Similar analyses of sediment records in the Florida Everglades indicate an increasing trend up through the decade of the 1980’s (Rood, *et al.,* 1995, Delfino, *et al*., 1993, 1994).

The most recent data on mercury trends at a site broadly representative of the continental U.S. was recently published by a team of USGS scientists (Schuster, et al., 2002). As shown in **Figure 1**, mercury has accumulated in core records since the Industrial Revolution, peaking in the 1960’s through the 1980’s and declining in the past decade or so.

A remaining area of great scientific uncertainty is how to incorporate the varying spatial scales of the atmospheric mercury cycle into an understanding of mercury bioaccumulation in aquatic systems. The differing chemical and physical forms of mercury found in the atmosphere vary greatly in their transport and deposition properties. Elemental mercury vapor {Hg(0)} is relatively inert and has an atmospheric half-life measured in months to years, exerting its effect world wide. Particulate-associated mercury {Hg(p)} has a half-life of days to weeks, exhibiting a regional effect (several hundred kilometers). Reactive gaseous mercury {RGM or Hg(II)} has a half-life measured in hours and, if emitted in this form, is deposited on a local scale, i.e. largely within a few score kilometers.

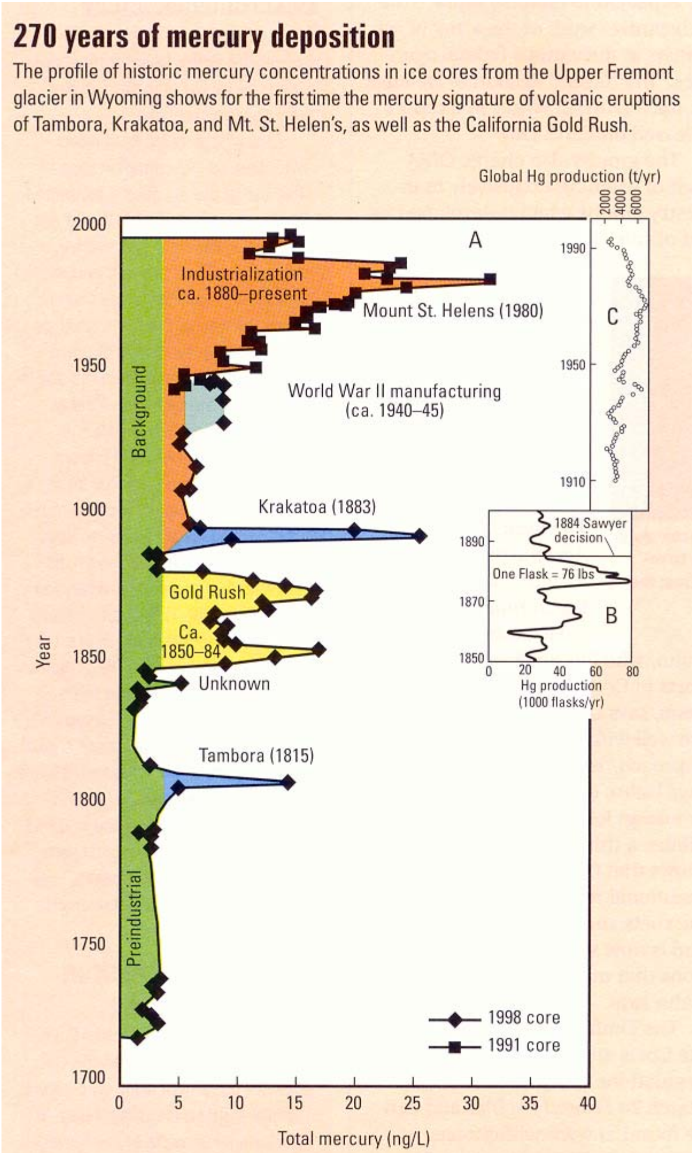

Figure 1. Long-term trends in mercury accumulation in ice cores from the Wind River Range, Wyoming, USA. Courtesy of USGS.

When looking at atmospheric loading from the frame of reference of a particular waterbody, the ability to distinguish global *vs.* regional *vs.* local scales of air transport and deposition is crucial to formulation of control strategy. Because of the geographic distribution of regional sources, and the fact that south Florida is meteorologically disjunct from the continental US, the scales important to the Everglades are local and global. This leads to the question: Is the source of mercury contributing to deposition into the Everglades predominantly coming from emissions sources within south Florida, or is it coming from long distance transport from sources around the globe? This pilot study asks: To what extent could abatement of south Florida mercury emissions reduce deposition on the Everglades and subsequent bioaccumulation in Everglades biota? This effort uses available data and mesoscale air and water models to address this question about local sources. It gives no direct information about the significance of global sources, which could limit the efficacy of local controls in reducing mercury concentrations in Everglades biota.

Although not directly relevant to the present analysis, which does not directly consider how global sources of mercury may affect Florida, it should be noted that complementary studies of mercury deposition in south Florida have yielded conflicting conclusions regarding the magnitude of global mercury sources. The present inability to directly gauge the relative importance of local vs. global sources, tells us that the scope of previous studies and some of the methods of sampling and analysis were limited in their ability to provide conclusive information. New, more specific and powerful methods have been developed, and are being applied in a series of studies over the next two years to ultimately enable us to answer this question with confidence.

2 PROBLEM STATEMENT

In 1989, monitoring by the Florida Fish and Wildlife Conservation Commission (FWC), the Florida Department of Environmental Protection (DEP), and the Florida Department of Health (DOH) revealed high levels of mercury in fish from the Everglades. Long known to be neurotoxic to humans, consumption of mercury-contaminated food had caused tragic illness and mortality in several episodes around the world. These findings led the Florida State Health Officer to issue Health Advisories urging fishermen not to eat some species of fish caught from the Everglades, and to limit consumption of largemouth bass and several other predatory fish species taken from many other fresh and coastal waters of Florida.

When extensive sampling was completed in the early 1990s, it was evident that approximately 1 million acres of the remnant Everglades system contained fish with high mercury burdens - largemouth bass averaged nearly 2.5 mg/kg mercury, which exceeded all health-based standards. More than another million acres of fresh waters in Florida contain largemouth bass with elevated but lesser levels of mercury. Were sampling to be comprehensive, we would expect mercury problems in bass to be found in one-half to two-thirds of Florida's waters. Florida DEP and USEPA have determined that inability to consume ones catch of sport fish at-will impairs recreation, a designated beneficial use of the affected waters.

This finding of excessive levels of mercury in fish is not limited to Florida. To date, over 40 states have issued health advisories restricting consumption of fish based on their mercury content, and similar problems are found broadly in North America, Europe and Asia.

2.1.1 Nature of the Everglades mercury problem

Mercury issues within the Everglades are extremely difficult to assess due to the size and heterogeneity of the Everglades, compounded by the complexity of mercury biogeochemistry. The gaps in scientific knowledge needed to control this problem are being addressed by a consortium of government and private agencies[2] collaborating as the South

[2] Florida Department of Environmental Protection, South Florida Water Management District, U.S. Environmental Protection Agency, Florida Electric Power Coordinating Group, Florida Fish and Wildlife Conservation Commission, and U.S. Geological Survey. Other SFMSP collaborators include the Academy of

Florida Mercury Science Program (SFMSP). The SFMSP goal is to elucidate the processes governing the environmental cycle of mercury through monitoring, modeling and research and to recommend sound management strategies for the mercury problem.

It is now generally accepted that this widespread mercury problem is caused by human activities that result in air emissions of mercury. Major sources to the atmosphere are municipal waste combustors (MWC), medical waste incinerators (MWI), metals mining and smelting; coal-fired utilities and industry; and the mining, smelting, use and disposal of mercury itself. The unusually severe problem in the Everglades has many unique features, and may be the result of a combination of factors (SFWMD, 1999, 2000, 2001, 2002). Both long distance transport and localized deposition around certain types of sources are important. The principal concerns there focus on local effects of waste incinerators and other emissions sources in southeast Florida, increased release of mercury or other substances from the Everglades Agricultural Area promoted by drainage and soil disturbance, or hydrologic changes.

The SFMSP has sponsored a series of projects related to this issue such as the Florida Atmospheric Mercury Study (FAMS), South Florida Atmospheric Mercury Monitoring Pilot Study (SoFAMMS), Florida Everglades Dry Deposition Study (FEDDS), Speciated Atmospheric Mercury Study (SAMS), USEPA Regional Environmental Monitoring and Assessment Program (REMAP), Speciated Atmospheric Mercury Profiling Experiment (SAMPEX) and the USGS Aquatic Cycling of Mercury in the Everglades (ACME) program. Numerous publications have resulted[3]. The South Florida Water Management District and the Florida Fish and Wildlife Conservation Commission (FWC) also have ongoing monitoring programs. Data from these programs were used extensively to develop and calibrate the models applied in this assessment.

2.1.2 Rationale for a TMDL approach

From its inception, the SFMSP approached the Everglades mercury problem as a multimedia one. The conceptual model encompassed three major processes – atmospheric sources and cycling, aquatic cycling, and bioaccumulation – and the linkages between them. Components addressed in this analysis include sources of mercury, and environmental media including air, water, sediments, and biota.

When renewed emphasis on the TMDL process emerged in the late 1990's, the approach being taken by the SFMSP was compatible; thus further monitoring, modeling and research have been coordinated with the long-term goals of the TMDL approach. Because of the extensive data collected and models developed by the SFMSP through the 1990's, USEPA in 1999 solicited Florida's participation as one of two states for pilot studies of how to

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Natural Sciences of Philadelphia, Electric Power Research Institute, Florida International U., Florida Power and Light Co., Florida State U., National Oceanic and Atmospheric Administration, Oak Ridge National Laboratory, Texas A & M U. at Galveston, U. of Florida, U. of Miami, U. of Michigan, U.S. Fish and Wildlife Service, U.S. Army Corps of Engineers, and U.S. National Park Service.

[3] For a partial bibliography see: http://www.floridadep.org/labs/mercury/index.htm

rationally incorporate deposition of air pollutants in the TMDL process. Thus began what is termed the Florida Mercury TMDL Pilot Study.

For this project, we chose a site within Everglades Water Conservation Area 3A, Site 3A-15, because of the richness of data from that region (3A-15 was one of the USGS ACME intensive study sites, and there existed an extensive water quality database for the region from the USEPA REMAP project). This site was also known to have high concentrations of mercury in fish. It is important to recognize that, although the Everglades is widely recognized as a large freshwater wetland, it is by no means homogeneous; rather, it comprises a host of diverse environments of different types of vegetative assemblages and environmental gradients. Likewise, mercury concentrations in water, sediments, and biota also are spatially heterogeneous. Thus, the results from this pilot analysis cannot and should not be extrapolated to any other portion of the Everglades.

This pilot TMDL evaluates various scenarios of atmospheric emissions from point sources in south Florida and simulates the effects of these atmospheric loadings on bioaccumulation in top predators in the Everglades aquatic system. Key to the approach is the linkage of atmospheric deposition models (Hybrid Single Particle Lagrangian Integrated Trajectories Model, version 4 [HYSPLIT_4] and Regional Atmospheric Modeling System [RAMS]) with the Everglades Mercury Cycling Model (E-MCM) to estimate mercury concentrations in predatory fish (i.e., largemouth bass). Detailed reports containing the results of these models are provided as Appendices I and II to this document. A summary of the relevant results from the modeling efforts is provided in this report.

2.2 Description of TMDL Process

Water quality standards are established to protect the designated uses of Florida's waters. When States, Tribes or local communities identify problems in meeting water quality standards, a TMDL can be a framework for addressing those problems. The purpose of this demonstration project is to explore the utility of using atmospheric and mercury-cycling models within the TMDL framework and to provide the stakeholders with technical information that may be used to develop a water quality plan to address mercury issues in the Everglades.

Section 303(d) of the Clean Water Act (CWA) requires states to identify the waters for which the effluent limitations required under the National Pollutant Discharge Elimination System (NPDES) or any other enforceable limits are not stringent enough to meet any water quality standard adopted for such waters. The states must also prioritize these impaired water bodies for TMDL development, taking into account the severity of the pollution and the beneficial uses of the waters.

A TMDL represents the maximum amount of a given pollutant that a particular waterbody can assimilate without exceeding surface water standards. The TMDL can be expressed as the total mass of pollutant that can enter the water body within a unit of time. For this pilot TMDL, it is the total mass of atmospherically and water-borne mercury that enters the Everglades. In most cases, the TMDL determines the allowable mass per day of a pollutant and divides it among the various pollution sources in the watershed as waste load (i.e., point source discharge) and load (i.e., non-point source) allocations. The TMDL also accounts for natural background sources (e.g., atmospheric deposition derived from global sources) and provides a margin of safety.

Although this document is not a TMDL determination *per se*, we list the elements of TMDLs as described in USEPA guidance to put this pilot effort in context. Specifically, we discuss how this document compares with those elements, and in what additional elements work would be needed to fully develop a TMDL. Some of these elements are required under the Clean Water Act, while others are elements recommended in USEPA guidance. The following eight elements represent USEPA Region 4 TMDL guidance:

1. **Plan to meet State Water Quality Standards:** Although not explicitly required by the USEPA guidance for TMDL analyses, it is desirable to include a study and plan for the specific water and pollutants that must be addressed to ensure that applicable water quality standards are attained.

2. **Describe quantified water quality goals, targets, or endpoints:** The TMDL must establish numeric endpoints for the water quality standards, including beneficial uses to be protected, as a result of implementing the TMDL. This often requires an interpretation that clearly describes the linkage(s) between factors impacting water quality standards.

3. **Analyze/account for all sources of pollutants.** All significant pollutant sources are described, including the magnitude and location of sources.

4. **Identify pollution reduction goals.** The TMDL plan includes pollutant reduction targets for all point and non-point sources of pollution.

5. **Describe the linkage between water quality endpoints and pollutants of concern.** The TMDL must explain the relationship between the numeric targets and the pollutants of concern. That is, do the recommended pollutant load allocations exceed the loading capacity of the receiving water?

6. **Develop margin of safety that considers uncertainties, seasonal variations, and critical conditions.** The TMDL must describe how any uncertainties regarding the ability of the plan to meet water quality standards will be addressed. The plan must consider these issues in its recommended pollution reduction targets and must provide reasonable assurances that the appropriate load reductions will be implemented.

7. **Provide implementation recommendations for pollutant reduction actions and a monitoring plan.** The TMDL should provide a specific process and schedule for achieving pollutant reduction targets. A monitoring plan should also be included, especially where management actions will be phased in over time and to assess the achievement and validity of the pollutant reduction goals.

8. **Include an appropriate level of public involvement in the TMDL process.** This is usually met by publishing public notice of the TMDL, circulating the TMDL for public comment, and holding public meetings in local communities. Public involvement must be documented in the state's TMDL submittal to USEPA Region 4.

The elements of a TMDL required by statute are loading capacity, wasteload allocation, load allocation, margin of safety, and seasonal variation.

2.2.1 Current Status of addressing TMDL Elements

This analysis addresses of 5 of the 8 elements of the TMDL process, described below:

1. **Describe quantified water quality goals, targets, or endpoints**. The present quantitative endpoints for mercury in Florida waters derive from its propensity for bioaccumulation in aquatic food webs, presenting chronic health risks to humans and wildlife that eat large amounts of fish. The quantitative endpoints for human health are the DOH guidelines for mercury health advisories to fishermen, detailed in section 3.3 of this report, specifically in Table 4. Florida Department of Health guidelines for mercury in fish consumption advisories.
2. **Analyze and account for all sources of pollutants**. The primary sources of mercury to the Everglades are storm water runoff via canal structures draining into the Everglades, and atmospheric deposition. The data given in **Table 1** (USEPA, 2001) define the proximate sources of the mercury load to the Everglades Protection Area (i.e. the water conservation areas and ENP). However, until apportionment of the mercury deposition between local emissions and global background sources has been resolved, this element cannot be completed to the extent of formulation of source-specific controls.

Table 1. EPA Mercury Loading. Comparison of Atmospheric vs. Surface Water Loading to the Everglades Protection Area

Year	Atmospheric Deposition Hg kg/yr. [4]	EAA Water Discharge Hg kg/yr.[5]
1994	238	2
1995	206	3-4

3. **Identify pollution reduction goals.** The pollutant reduction goal here is the reduction of atmospheric mercury deposition necessary to achieve mercury deposition needed to achieve a concentration in Everglades fish of less than 0.5 mg/kg. Within the limitations of the assumptions of the air and water models, the pollutant reduction goal for atmospheric deposition from locally derived sources has been estimated.

[4] Annual deposition derived from Florida Atmospheric Mercury Study (FAMS), 1993 – 1996.
[5] Derived from biweekly monitoring of 'into' structures discharging from the EAA into the Everglades Protection Area, USEPA, 1994 - 1996.

4. **Describe the linkage between water quality endpoints and pollutants of concern**. This is described by the modeling presented in Chapter 4 of this analysis, which suggests a strong direct relationship between inorganic mercury loads to the Everglades Protection Area from atmospheric deposition (**Figure 9**) and mercury concentrations in largemouth bass. In addition, modeling suggests a relatively rapid response of mercury in fish to changes in load (**Figure 10**).
5. **Develop margin of safety that considers uncertainties, seasonal variations, and critical conditions**. A margin of safety could be incorporated into the analysis as regards a human health reference dose for mercury, and in the atmospheric and aquatic modeling. This issue is discussed more fully in Section 5.3.

Because this is a pilot TMDL, none of the elements of the TMDL methodology has been completely resolved in this report. Key portions of Elements 2 - 6 are addressed, but these must be treated more exhaustively in later analyses. Addressing Element 7 awaits narrowing the uncertainties highlighted here. Both external[6] and internal peer review of this pilot study have been completed; comments from various stakeholders – public, private and interested parties – have been incorporated herein. As this document is not a complete TMDL analysis, the stakeholder review for the pilot – Element 8 – was not intended to fulfill the public review requirements for a TMDL. Review comments and responses are summarized in Appendix III.

2.3 Florida's 303(d) Process

Florida's rivers, streams, and lakes are spectacularly beautiful and are essential natural resources, supplying water necessary for public consumption, recreation, industry, agriculture, and aquatic life (DEP, 2000). DEP is responsible for preserving and maintaining the quality of Florida's waters. The TMDL program is a key component of a comprehensive approach to protecting water quality in Florida. As directed by Florida Statues, rules have been developed to give specific guidance for implementing the TMDL process. Rule 62-303, F.A.C (Impaired Waters Rule) defines the data and methodologies required for placing waterbodies on the impaired list.

DEP has developed a five-phase approach to eliminating water quality impairment through its 303(d) Process (Table 2). This integrates monitoring and evaluation on a five-year cycle to assess quality of all waters. Waterbodies listed in earlier assessment cycles have been placed on a 'planning list,' whereby further monitoring is initiated to validate the original listing and determine probable sources of the stressors causing the listing. This monitoring step was added because waters often were originally listed based on nominal data and information. The data analysis step provides detailed documentation of the water quality and serves as the basis for the development of the TMDL for waterbodies on the validated list.

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[6] The first draft of this report was submitted to an independent panel for review. Those reviewers were:
Dr. Mark Cohen, NOAA Air Resources Laboratory
Dr. Kent Thornton, Principal Ecologist, FTN Associates, Ltd.
Dr. Joseph V. DePinto, LimnoTech, Inc.
Dr. Donald B. Porcella, Environmental Science and Management, Electric Power Research Institute
Dr. Robert P. Mason, Associate Professor, Chesapeake Biological Laboratory, University of Maryland

The TMDLs and other basin related issues are incorporated into a Basin Management Plan in consultation with local stakeholders. When water quality impairment is found, TMDL assessments are initiated.

Table 2. Steps in Florida's 303(d) Process
1. Initial Basin Assessment. Identification of waterbodies requiring restoration, protection, or TMDL development.
2. Coordinated Monitoring. Supplement existing data for TMDL development
3. Data Analysis and TMDL Development. Document water quality and conduct TMDLs
4. Basin Management Plan Development. Work with local stakeholders Incorporate implementation of TMDLs Address watershed goals
5. Begin Implementation of Basin Management Plan.

If additional data or closer examinations of existing data show that the water quality is impaired, then the most appropriate action to bring this water body back into compliance with its standard is pursued. Typically, this action would include completing a TMDL analysis for the drainage basin.

Changes in standards or the establishment of site-specific standards are the result of ongoing science-based investigations or changes in toxicity criteria from USEPA. Changes in designated uses and standards are part of the USEPA's surface water standards triennial review process and are subject to public review. Standards are not changed simply to bring the water body into compliance, but are based on existing uses and natural conditions.

Seventeen areas of the Everglades are included on Florida's 1998 Water Quality Limited Waters List (303(d) List) for violations due to fish consumption advisories for mercury, including WCAs 1, 2, 3, and Everglades National Park (ENP). The project study area, WCA 3A-15, is listed for fish consumption advisories for mercury (**Figure 2**).

2.4 Watershed

2.4.1 Overview

The Everglades are a naturally occurring wetland system that historically (i.e., prior to 1855) occupied the lower third of the Florida peninsula south of Lake Okeechobee (**Figure 2**). Hydrologically, the Everglades are part of the greater Kissimmee River-Lake Okeechobee-Everglades system that conveyed water from central Florida southward towards Florida Bay.

Water flowed southward through a "ridge and slough" landscape that consisted of sloughs, channels, sawgrass ridges, and tree islands (SFWMD, 1992a, 1992b, 1999, 2000, 2001).

During the 20th Century, the extent of the Everglades was significantly reduced and the spatial and temporal patterns in hydrology, fire, and nutrient supply altered (Davis and Ogden, 1994). Approximately half of the Everglades were drained for agriculture and urban development during the early to mid 20th Century. Presently, the north to south movement of water through the remnant Everglades is regulated by control structures at Lake Okeechobee and in the Water Conservation Areas (**Figure 2**).

GIS coverages for land use, land ownership, and vegetation types were obtained from BASINS2 (USEPA, 1998). Land usage is based on the Anderson Level 2 land classification system. Topographic information was obtained from BASINS2 (1:250,000 scale DEM).

2.4.2 Hydrology

The present Everglades system extends from the southern edge of Lake Okeechobee through the Everglades Agricultural Area (EAA), Water Conservation Areas and Everglades National Park to Florida Bay. The EAA has been diked and drained to supply land for agriculture. Water flows slowly in a southerly direction from Lake Okeechobee. The overall topographic gradient between Lake Okeechobee and Florida Bay is approximately 1 foot per 10 miles (0.3 m/16.1 km) (Davis and Ogden, 1994).

WCA-3A is contained by levees on three sides. On the western side it is only partially leveed to allow overland water flow from the Big Cypress swamp (Davis and Ogden, 1994). Major water inputs are from the S-11 structures (A, B, & C) and the S-8 and S-9 pump stations on the Miami Canal and the S-140 pump station that drains from Hendry County. Gravity drainage from the S-150 spillway also occurs at times. Within WCA-3A, ground elevation ranges from 7 to 10 feet above Mean Sea Level (Davis and Ogden, 1994).

Rainfall supplies approximately 70 percent of the annual water budget of the Water Conservation Areas (Davis and Ogden, 1994). The remainder comes from runoff from the EAA. Long-term average annual precipitation near WCA 3A ranges between 51.6 inches at a station near Lake Okeechobee, to 50.4 inches in the ENP (SERCC, 2000). During the period between 1970 and 1998, the station located at WCA 3A-S_R averaged 50.3 inches per year (SFWMD, 1999). The highest precipitation occurs from June through September with between 6 and 9 inches of rainfall per month. The winter months are considerably drier, with rainfall approximately 1 inch/mo.

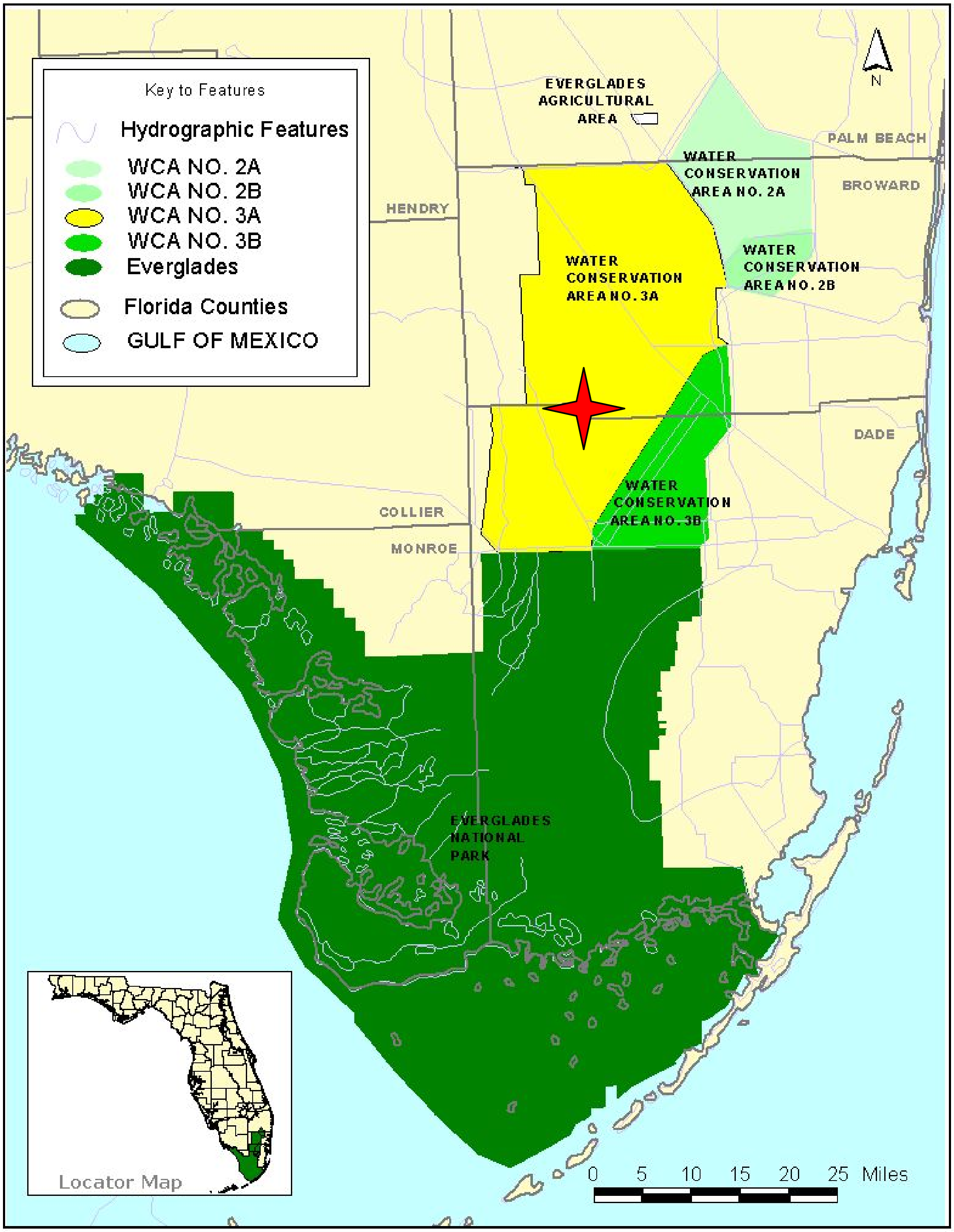

Figure 2. Location of Everglades watershed, Water Conservation Area 3A, and study site 3A-15.

The annual ambient air temperature is between 72 and 75 ^{o}F (22 – 24 ^{o}C), varying from an average monthly temperature of 62 to 66 ^{o}F (16.7 - 19 ^{o}C) in January to an average of 80 to 83 ^{o}F (26.7 - 28 ^{o}C) in August (SERCC, 2000). Minimum temperatures for January averaged 52^{o}F (11 ^{o}C), and maximum temperatures for August averaged 91^{o}F (32.8^{o}C) between 1961 and 1990 (SERCC, 2000).

2.4.3 Physiographic Characteristics

Land elevations change only subtly throughout the Everglades. The average slope between Lake Okeechobee in the north and Florida Bay in the south is approximately 1:53,700 (Davis and Ogden, 1994).

Everglades soils consist predominantly of peat soils underlain by limestone deposits.

2.4.4 Vegetation and Land Use

WCA-3A is predominantly composed of wetlands dominated by herbaceous plants (95%), of which approximately 50% is comprised of sawgrass and cattails, approximately 45% is wet prairies, and some forested wetland areas (3.5%) do occur. Evergreen forests, mixed rangeland, and localized built-up areas make up the remaining 1.5 percent of the area (BASINS2, USEPA, 1998).

WCA 3A provides flood protection and water supply to residents in southeast Florida. In addition, this area provides fish and wildlife habitat as well as recreational opportunities (e.g., fishing).

2.5 Existing Conditions and Summary of Monitoring Data

Several water quality parameters have been identified as having an impact on concentrations of total and methylmercury in freshwater systems. In particular, dissolved organic carbon, pH, sulfate (and sulfide), and chloride have received much attention. Table 3 shows the average values for water quality parameters at WCA 3A-15.

Mercury concentrations were measured in surface waters at WCA-3A-15 on 8 occasions between 1995 and 1998. Total mercury ranged from 1.05 ng/L to 2.70 ng/L and averaged 1.94 ng/L (Krabbenhoft, *et al.*, 1998). Largemouth bass (*Micropterus salmoides*) were collected at WCA 3A-15 on 5 occasions between December 1996 and November 1998 by the FWC (Lange, *et al.*, unpublished data). Fish ranged in length from 12 cm to 51 cm. Mercury concentrations in the tissue ranged from 0.45 mg/kg to 4.3 mg/kg (**Figure 3**).

Table 3. General Water Quality Characteristics of WCA 3A-15.	
Parameter	Value
Dissolved organic carbon	~ 16 mg/L
Surface water pH	~ 7.2
Surface water chloride	~ 5 mg/L
Surface water sulfate	100 μeq/L
Sedimentation rate	< 1 cm/yr.
Total suspended solids	~ 2 mg/L
Fraction of marsh with open water	<50%
Periphyton density	High
Macrophytes	Includes sawgrass, cattails, water lilies

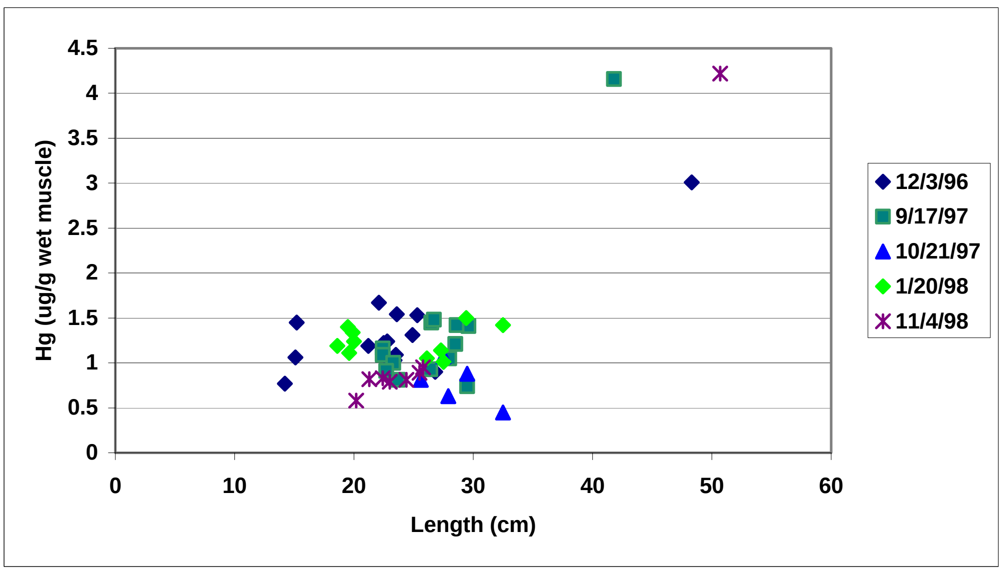

Figure 3. Methylmercury concentrations in largemouth bass in WCA 3A-15. (Lange, *et al.* unpublished data).

2.6 Identification of Violated Water Quality Standards and Impaired Designated Uses

Under the federal Clean Water Act, states are responsible for establishing, reviewing, , and revising water quality standards. The components of the surface water quality standards system include: classifications, water quality criteria, an antidegradation policy, and special protection of certain waters. Florida has five classes of waters with associated designated uses, which are arranged in order of degree of protection required:

Class I - Potable Water Supply
Fourteen general areas throughout the state including: impoundments and associated tributaries, certain lakes, rivers, or portions of rivers that are used as a drinking water supply.

Class II - Shellfish Propagation or Harvesting
Generally coastal waters where microbial water quality allows for commercial shellfish harvesting.

Class III- Recreation, Propagation and Maintenance of a Healthy, Well-Balanced Population of Fish and Wildlife
The surface waters of the state are Class III unless otherwise described in rule 62-302.400 of the Florida Administrative Code. These uses are also protected for all Class I and Class II waters.

Class IV- Agricultural Water Supplies
Generally located in agriculture areas around Lake Okeechobee.

Class V - Navigation, Utility and Industrial Use
Currently, there are no Class V water bodies.

To protect the present and future most beneficial uses of these waters, water quality criteria have been established for each classification. While some of these criteria are intended to protect aquatic life, others are designed to protect human health. Water quality standards, described in Rules 62-302.500 and 62.302.530, F.A.C, are expressed as either numeric (a specific concentration which cannot be exceeded) or narrative (used to describe a condition that is not desired). All of the Everglades, including Water Conservation Area 3A, is classified as a Class III water body. This designation means its waters are to be suitable for recreation, and propagation and maintenance of a healthy, well-balanced population of fish and wildlife.

Florida's Class III water quality criterion of 12 ng/L for total, unfiltered mercury has not been exceeded in either the Everglades marsh, or in tributary waters. However, the Department of Health (DOH) fish tissue guidance concentration of 0.5 mg/kg is currently exceeded throughout areas of the marsh, prompting the issuance of fish consumption advisories by the Florida State Health Officer. DEP recognizes that health advisories impair recreation and that this means that the current water quality criterion, which is met, is of limited utility.

Furthermore, as regards protection of Everglades wildlife, risk assessments conducted by the SFWMD (Fink *et al*., 1999) as part of the South Florida Mercury Science Program have identified the potential for adverse effects from mercury for wading birds. A preliminary risk assessment for the Florida panther (*Felis concolor coryi*, a Federally-listed endangered species), indicates that this species may be at risk from methylmercury, particularly in areas where panthers consume prey that feed on fish-eating wildlife.

Detailed discussions of the atmospheric and aquatic fate and transport processes are provided in the modeling technical support documents (Keeler, *et al.*, 2001; Tetra Tech, 2001) prepared to support this analysis. These documents are provided as Appendices I and II.

2.7 Identification of Pollutants Being Addressed and Why

This TMDL addresses the trace element mercury in its various environmental forms. The behavior of mercury in the environment is highly complex with each of the several chemical forms behaving differently. Methylmercury, formed from inorganic mercury by sulfate-reducing bacteria in the sediments is the most biologically active form. Once formed, methylmercury is readily taken up and retained by organisms and tends to increase in concentration in higher trophic levels (i.e., biomagnifies). Although at ambient levels methylmercury does not appear to significantly affect plants, invertebrates, or fishes, when biomagnified, as in the Everglades 1 to 10-million fold, it poses the risk of chronic neurotoxicity to birds and mammals, including humans.

Previous work in the Everglades has shown that the dominant input of mercury (95%) to the WCA 3A is from atmospheric sources (USEPA, 1998; SFWMD, 1999). The remainder of the mercury enters the system via overland flow from tributary watersheds.

3 NUMERIC TARGETS AND WATERSHED INDICATORS

This section identifies the selection of water quality targets for the TMDL. An objective of a TMDL is to define a safe concentration, in this case, of mercury. Additionally, this section develops a source allocation (air and water) that will allow the water quality goal to be met.

3.1 Numeric Targets

Because of the biogeochemical cycling of mercury between the earth and the atmosphere, and because many factors affect its availability and propensity for bioaccumulation, mercury poses unique problems in setting numeric targets. No simple relationship links mercury concentrations in water and mercury concentrations in fish; the relationship is site specific.

Using previous (1984) USEPA guidance, Florida in 1992 adopted a Class III water quality criterion for total (unfiltered) mercury of 12 ng/L, which was believed adequate at the time to prevent excessive mercury accumulation in fish such that these fish could be consumed without concern as regards human health effects. Subsequent studies have shown that mercury levels in fish exceed the DOH consumption advisory level of 0.5 mg/kg in many waters that met the Class III water quality criterion, including most of the Everglades. The Florida Department of Environmental Protection has determined that the inability of anglers to eat their catch at-will impairs recreation, a designated use of Class III waters. Through its participation in the SFMSP and this TMDL study, DEP is working to develop sufficient information to establish a mercury criterion that will protect all of the beneficial uses.

Since it is fish mercury levels rather than mercury concentrations in water that have the potential to impair both the recreational use and protection of fish and wildlife designated uses of Class III Florida waters, a fish mercury level is a more appropriate criterion for this pilot project. A fish mercury criterion integrates those site-specific biogeochemical and food web effects that result in bioaccumulation. While prediction of fish mercury levels from atmospheric loading is a complex endeavor, it is not significantly more complex that predicting mercury concentrations in water, and it is a far better indicator of effects on beneficial uses. In recognition of this, in 2000 the USEPA issued a new human health methylmercury criterion as a fish tissue criterion.

For this TMDL pilot project, a numeric target of 0.5 mg/kg total mercury in age 3 largemouth bass has been selected, as this is currently the level which Florida uses as the basis for fish consumption advisories. Whether this numeric target is protective of human health or wildlife populations awaits further review (see below).

3.2 Identification of Watershed Indicators

Mercury concentration in the edible flesh of fish determines whether the recreational use of a waterbody is impaired. Mercury concentration in prey fish determines whether the fish and wildlife use is impaired. The indication of impairment in wildlife is wildlife daily dietary mercury consumption in comparison to the maximum, safe daily dose. The maximum, safe daily dose is not known for any Everglades species, but is inferred with unknown uncertainty for wading birds from mallard duck feeding studies. Safe daily dose must be determined for the species of interest and compared with actual exposure. Without this information, there is no basis for establishing a margin of safety.

3.3 Identification of Target Levels to be Protective of Beneficial Uses

The Everglades Protection Area (i.e. the water conservation areas and ENP) are designated as Class III waters of the State, which are to be protected for recreation and for the propagation and maintenance of a ‘healthy, well-balanced population of fish and wildlife.’

Following the finding in 1989 of elevated levels of mercury, the Florida Department of Health, Toxicology and Hazard Assessment Section, surveyed the literature and consulted toxicologists in other states as to risks posed to fishermen and their families. DOH developed advisories to the public in general accord with exposure limits then recommended by the World Health Organization and other states. Since the late 1980’s, several studies, re-analyses and meta-analyses have been conducted to further refine estimates of acceptable human exposure to mercury.

In its Mercury Study Report to Congress (USEPA, 1997), USEPA proposed lowering its ‘reference dose’ for methylmercury from 0.3 μg/kg body weight/day to 0.1 μg/kg body weight/day. Congress referred this risk assessment to the National Research Council for independent review, and in 2000 the National Research Council gave substantial support to the new USEPA reference dose. Subsequently, in late 2000, USEPA published a new recommended water quality criterion for mercury of 0.3 mg/kg, expressed as methylmercury in fish flesh. This recommended criterion will be considered in due course by DEP through the Clean Water Act mandated Triennial Review process.

Pending reevaluation of standards, Florida DOH guidelines (Clewell, et al., 1998) for acceptable concentrations of total mercury in the edible portions of wild-caught fish are those given in Table 4.

Table 4. Florida Department of Health guidelines for mercury in fish consumption advisories.

Advisory	Mercury Concentration
See information provided by USEPA below [7]	Less than 0.5 mg/kg
Limited Consumption – fish should not be eaten more than once per month by women of childbearing age or children, nor more than once per week by other adults.	0.5 to 1.5 mg/kg
No Consumption – fish should not be eaten	Greater than 1.5 mg/kg

Note from **Table 4** that fish tissue total mercury concentrations greater than 0.5 mg/kg result in the establishment of fish consumption advisories. (For high trophic level fish, such as largemouth bass, total mercury and methylmercury concentrations are essentially equivalent.) DEP has made the determination that recreational use necessitates that fish not only be present and available to anglers, but also that these fish must be safe to eat.

Mercury concentrations in fish tissue currently exceed the 0.5 mg/kg fish consumption advisory level throughout the Everglades/Big Cypress system, and exceed the 1.5 mg/kg level in parts of Water Conservation Areas 2, and 3, and in the freshwater portions of Everglades National Park.

Mercury bioaccumulates in the aquatic food chain. Therefore, top predators such as the largemouth bass can be expected to accumulate the greatest concentrations of mercury. This pilot TMDL uses the Florida DOH guideline for acceptable mercury concentration in fish of 0.5 mg/kg in 3-year-old largemouth bass as the numeric target, because this is currently the level that Florida uses as the basis for fish consumption advisories. Three-year-old (*ca.* 1000 g) bass were selected as the appropriate index of ingestion exposure because this size class is legally harvestable, abundant, and is the most prevalent cohort in the angler's catch (F. Ware, personal communication).

The pilot TMDL study indicates that mercury from atmospheric deposition needs to be reduced to achieve the desired fish tissue concentration. The target range for mercury and possible strategies for attaining the desired levels of mercury are provided in Chapter 4 *Air and Watershed Modeling* and Chapter 6 *Conclusions, Research Needs and Plans*, of this report.

[7] The USEPA recommends women of childbearing age eat no more than 8 ounces of freshwater fish caught by family and friends in a week's time period; children under 10 should eat no more than 4 ounces. For further details on the EPA advisory see world wide web: http://www.epa.gov/ost/fishadvice

3.4 Comparison of Numeric Targets and Existing Conditions

This section assesses how far the water quality parameters of concern for WCA 3A must change in order to comply with the stated water quality standards for the water body. **Table 5** gives the existing water quality conditions, the desired water quality endpoints, and comments.

Table 5.
Comparison of Existing Conditions to Water Quality Endpoints

Parameter	Existing Value (Mean and range)	Water Quality Endpoint	Comments
Mercury in ambient water (ng/L)	1.94 (1.05 – 2.70)	Florida Class III Water Quality Standard: < 12ng/L	This value is designed to ensure that water standards are met.
Mercury in edible sport fish tissue (mg/kg)	1.28 (0.45 – 4.3)	Florida DOH fish consumption advisory: < 0.5 mg/kg	Concentrations greater than this value trigger the issuance of fish consumption advisories by DOH.
Mercury in whole prey fish (mg/kg)	0.1 mg/kg provisional USFWS standard	Safe tissue concentration for propagation and maintenance of a healthy, well-balanced population of fish and wildlife	This value is estimated to be protective of fish-eating wildlife and animals that feed on them.

4 AIR AND WATERSHED MODELING: SOURCE ANALYSIS FOR LOADINGS, MERCURY MASS BALANCE, LINKAGE OF STRESSORS TO WATER QUALITY ENDPOINTS

This section summarizes the methods and results of the atmospheric modeling (Keeler *et al.*, 2001) and aquatic mercury cycling (Tetra Tech, 2001) modeling efforts used in this project. Full details of the modeling efforts can be found in the Technical Reports provided as Appendix I (Atmospheric Model) and Appendix II (E-MCM) of this report.

There are four primary forms of mercury considered in the models: three of these are methylmercury {MeHg}, divalent mercury salts and compounds {Hg(II)} and elemental mercury {Hg(0)}. Hg(II) is explicitly defined here as all divalent inorganic mercury (other than particulate associated divalent inorganic mercury). The fourth form is Hg(p) representing divalent inorganic mercury {Hg(II)} that is associated with suspended particulate matter in water or air. Provisions have also been made in the E-MCM for some of the particulate Hg(II) on non-living solids in water to exchange slowly, while the remainder is assumed to exchange rapidly enough to assume instantaneous partitioning.

4.1 Technical Approach

Two modeling components were employed for this project. The first modeling approach, developed by the University of Michigan Air Quality Laboratory (UMAQL), was used to simulate the atmospheric transport of mercury from point sources in southern Florida to its deposition onto the Everglades (Keeler, *et al.*, 2001; Appendix I). The second model, the Everglades Mercury Cycling Model (E-MCM), was used to simulate the fate and transport of the mercury within the aquatic environment (Tetra Tech, 1998, 2001; Appendix II). The E-MCM provides estimates of the rates of mercury methylation and bioaccumulation through the food chain to a top-level predatory fish (largemouth bass). Detailed descriptions of these models and uncertainties are provided in the referenced technical support documents for this analysis.

4.1.1 Source Analysis of Loadings

Sources evaluated in this study include both atmospheric emissions and surface water inputs of mercury. The atmospheric source characterization was based on the emissions database used for the RELMAP (Bullock, *et al.*, 1997) modeling simulations performed for the USEPA Mercury Study Report to Congress (USEPA, 1997). The USEPA mercury emissions database includes speciated data for both area- and point-source emissions, with a summary of the standard speciation profiles used for point-source emissions listed in **Table 6. Figure 4** shows the location and relative magnitude of the 38 point sources considered in this analysis. The analysis of Dvonch, *et al.*, (1999) utilizing receptor modeling and emissions inventory scaling techniques, estimated the importance of local mercury sources potentially impacting south Florida. That analysis indicated that approximately 92% of the total mercury deposition to south Florida could be accounted for by local sources alone. Thus, this analysis was limited to Florida sources and a complete listing of the point sources used in this study can be found in **Table C1** of Appendix I. The USEPA mercury emissions database considered 'area source' emissions to be only mercury in the elemental form, Hg(0), and these accounted for only 2 percent of the total emissions. As a result, area sources were not considered in this study.

Table 6.
Mercury Speciation Percentages Used In Current Study

Mercury Emission Source Type	Speciation Percentages		
	Hg(0)	Hg(II)	Hg(p)
Municipal Waste Combustion	20	60	20
Medical Waste Incinerators	2	73	25
Electric Utility Boilers (coal, oil, gas)	50	30	20
Commercial and Industrial Boilers	50	30	20
Hazardous Waste Incinerators	As specified per location in USEPA database		

Mercury inputs to WCA 3A-15 via surface water flow were based on data collected as part of the USGS ACME study (Krabbenhoft, *et al.*, 1998, *et al.*, 1998, Hurley, *et al.*, 1998, Cleckner, *et al.*, 1998). For these studies, surface water was collected at several sites, including site 3A-33, located *ca.* 50 km upstream of 3A-15, for analysis of total and methylmercury. The average concentrations of unfiltered Hg(II) and unfiltered methylmercury at 3A-33 were 2.14 and 0.27 ng/L respectively for 7 sampling dates between December 1996 and November 1999 [unfiltered Hg(II) is derived as the difference between measured Hg_{tot} and unfiltered MeHg]. These concentrations were assumed to be the surface inflow concentrations for site 3A-15.

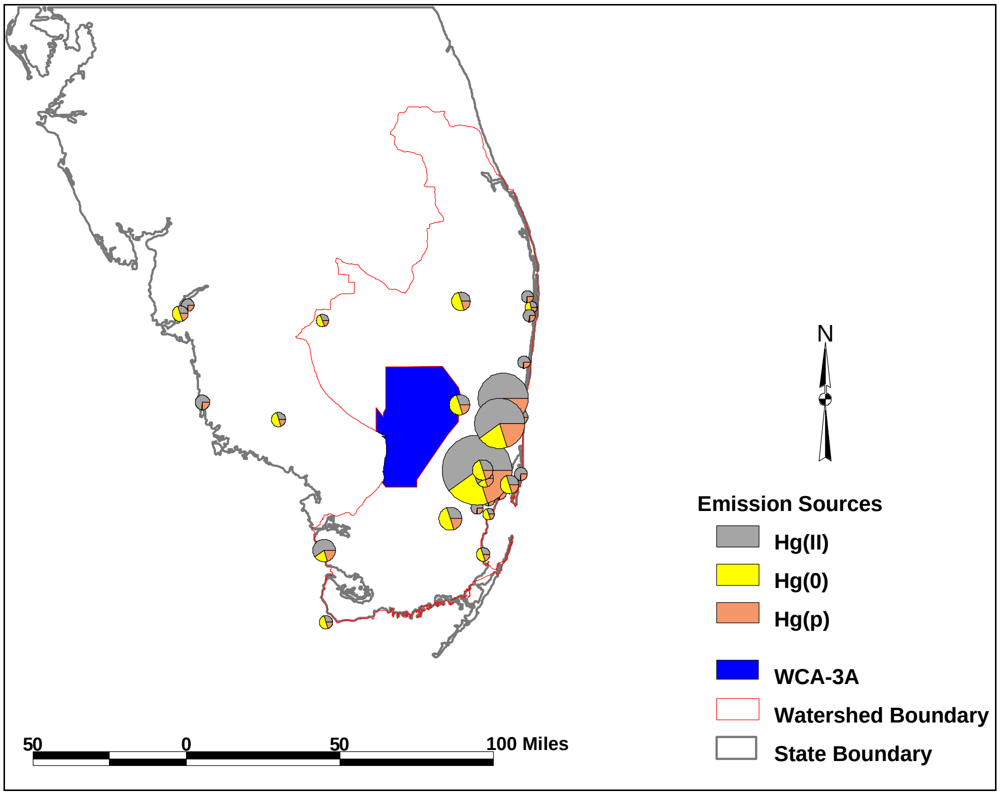

Figure 4. Locations and relative magnitudes of atmospheric point sources of mercury in south Florida.

4.2 Atmospheric Transport and Deposition Modeling

4.2.1 Approach Overview

The modeling conducted by UMAQL to link local emissions of mercury with deposition in south Florida and at site 3A-15 involved a 'hybridized' modeling approach (**Figure 5**). Two types of models were used to ultimately obtain estimates of the monthly and annual wet- and dry-deposition of speciated mercury {Hg(0), Hg(II) and Hg(p)} to the South Florida Water Management District's Water Conservation Area 3A (SFWMD WCA-3A). The first was a mesoscale meteorological model (Regional Atmospheric Modeling System {RAMS}; Pielke, *et al.*, 1983), which provided the meteorological components driving and influencing air parcel transport and mercury species deposition. The second was a Lagrangian air-pollution dispersion/deposition model to estimate average wet- and dry-deposition patterns and amounts (HYbrid Single Particle Lagrangian Integrated Trajectories Model Version 4 [HYSPLIT_4]; Draxler and Hess, 1997). Because simulating every day of the year-long study period would be prohibitively time- and resource-intensive, a clustering approach was adopted to identify distinct meteorological flow regimes which would likely lead to distinct wet- and dry-deposition patterns. Weighting each cluster by its annual frequency of occurrence in turn yielded an estimate of monthly and annual deposition.

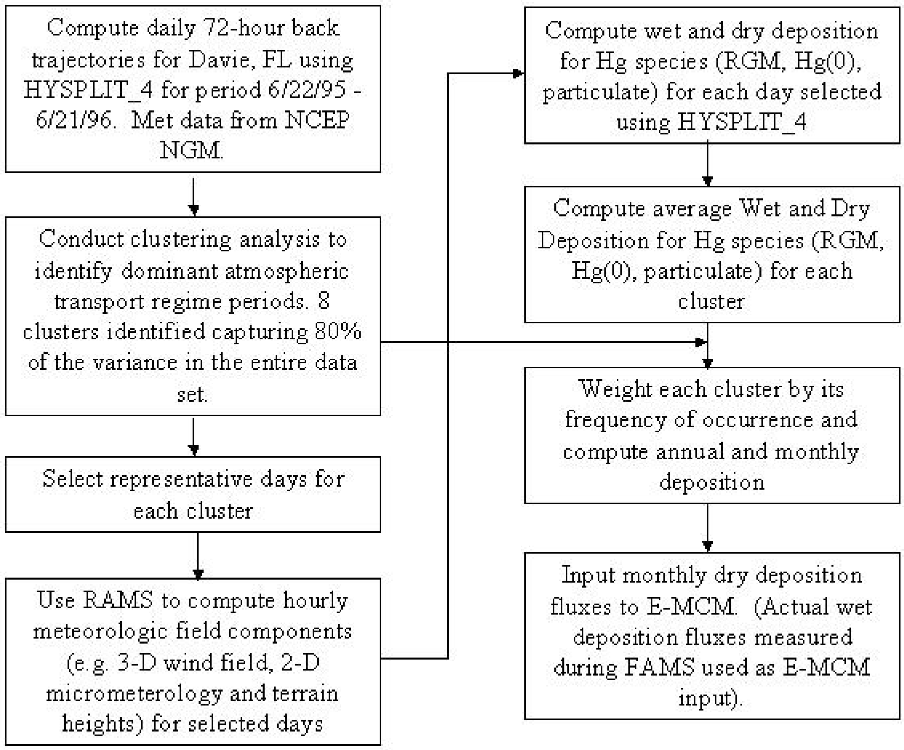

Figure 5. Schematic depiction of hybridized meteorological-atmospheric dispersion, transport and deposition modeling approach used to simulate Hg deposition in the WCA-3A by UMAQL. RGM is reactive gaseous mercury, believed to be Hg(II).

The specific steps employed in this hybrid approach are as follows:

(1) Compute daily back-trajectories (for air parcels arriving in Davie, FL) for each day of a one-year study period (22 June 1995 to 21 June 1996) during which precipitation was collected on an event (i.e., daily) basis at the University of Florida Agricultural Experiment Station in Davie, FL.
(2) Identify meteorological clusters, or groups, of back-trajectories that represent the dominant atmospheric transport regimes that impacted south Florida during the one-year study period.
(3) Select a number of representative days from each cluster and use RAMS to obtain hourly three-dimensional meteorological fields (U and V wind components, vertical velocity, temperature, specific humidity and pressure) and two-dimensional meteorological fields (terrain height, mean sea-level pressure, total precipitation, pressure, temperature, and micrometeorological parameters, which include u*, t* and q*) for the selected representative days.
(4) Using the three-dimensional and two-dimensional meteorological fields computed in part (3) as input fields; use HYSPLIT_4 to estimate average wet- and dry-deposition patterns/amounts for each of these representative days, computing a cluster average deposition for each of the clusters. HYSPLIT_4 was modified by UMAQL to

incorporate both basic mercury physical parameters and chemical processes, and include the ability to simulate the fate of the various mercury species important in the atmospheric deposition of mercury.

(5) Weight the average daily wet- and dry-deposition estimates for each cluster by the number of days assigned to each cluster, and thus obtain an estimate of the speciated monthly and annual wet- and dry-depositional loading of mercury to the SFWMD WCA-3A.

As mentioned above, climatological records for the one-year period from 22 June 1995 to 21 June 1996 were used to characterize the climatological conditions in the Everglades. This period was chosen as the 'year of record' because precipitation chemistry for mercury had been collected on an event (i.e., daily) basis at the University of Florida Agricultural Experiment Station in Davie, FL. How representative this one-year meteorological record was relative to the overall meteorologic regime of the area was investigated as part of this study (Keeler, *et al*., 2001). The results indicated that the study year was indeed representative of meteorological conditions over the eight-year period from 1991-1999, in terms of the frequency of the 8 meteorological clusters. However, average precipitation depth for 3 south Florida FAMS sites was 156 cm, somewhat higher than the long-term average range of 125 – 140 cm.

The input data used for the calculation of the daily back-trajectories consisted of analysis of short-term forecasted meteorological fields from the National Center for Environmental Prediction's (NCEP) Nested Grid Model (NGM). The standard NGM model domain encompasses the contiguous United States and Canada with a latitudinal and longitudinal grid spacing of approximately 90 km.

Early research suggested that the atmospheric deposition of mercury to south Florida is dominated by wet deposition, with the majority of this deposition associated with summertime convective precipitation events (Guentzel *et al.*, 2001, Dvonch *et al.*, 1999). The convective events responsible for the preponderance of wet deposition typically occur during the mid- to late-afternoon hours in south Florida and thus daily back-trajectories were calculated for 2000 GMT each day. The modeled analysis of dry deposition conducted as part of this study, however, suggests that dry deposition is important as well, comprising perhaps 34 to 40% of the total mercury deposition signal.

A number of previous regional atmospheric modeling studies have employed objective analyses of meteorological flow regimes to assess annual impacts from briefer intensive studies. Cluster analysis is an objective mathematical technique whereby large data sets can be divided into similar groups or clusters that reflect some underlying structure within the data set. For this analysis, the goal was to identify meteorological flow regimes which would likely lead to distinct wet- and dry deposition patterns. Weighting each cluster by its monthly and annual frequency of occurrence results in an estimate of the monthly and annual deposition without the necessity of modeling every day of the 1-year period studied.

Following the completion of the objective clustering of the back-trajectories, Daily Weather Maps from NOAA were used to evaluate each day of the year-long period to determine if the clustering resulted in an accurate representation of meteorological flow regimes. This hand analysis of the daily maps provided independent validation of the trajectory clustering approach.

Eight different atmospheric transport clusters were obtained through this analysis procedure, and a summary of these is presented in **Table 7**. For each meteorological cluster, the measured rainfall depth, volume-weighted mean mercury concentration, and the total mercury wet deposition are given from the Davie Monitoring site. The efficacy of the clustering technique is evident, with Meteorological Clusters 3 & 6 resulting in the majority of wet deposition of mercury. This data provides impetus for continuation of the hybrid modeling using the clustering and aggregation approach described later. Plots showing the general nature of each of the clustered back-trajectory groups can be found in Appendix A of Appendix I. Maps of the surface meteorological features for days representative of each cluster can be found in Appendix B of Appendix I.

Table 7.
Summary of "clustered" atmospheric transport regimes and precipitation statistics associated with each cluster based upon data collected at Davie, Florida during the 1995-96 SoFAMMS study period.

Cluster Number	Description of flow regime represented	No. of Days within cluster	No. of Days with Rainfall (Davie, FL)	Total Rainfall for Cluster (cm) (Davie, FL)	Volume Weighted Mean Hg Concentration for Cluster (ng/L) (Davie, FL)	Total Hg Wet deposition observed ($\mu g/m^2$) (Davie, FL)
1	Weak local flow, variable in direction	65	18	12.1	31.8	3.84
2	Weak synoptic flow from north	35	5	2.7	29.2	0.79
3	Moderate local/synoptic flow from east	104	30	26.2	20.9	5.47
4	Strong synoptic flow from northeast.	48	8	22.1	10.8	2.39
5	Strong synoptic flow from northwest	32	9	6.9	10.6	0.73
6	Moderate synoptic flow from south	58	29	94.0	14.5	13.64
7	Moderate synoptic flow from southwest	11	4	8.7	12.8	1.12
8	Strong synoptic flow from north	13	1	0.1	7.1	0.01

For each cluster, two wet days and two dry days were selected for use in the modeling exercise (**Table 8**). Where possible, these days were chosen such that they represented extremes in the spatial nature of the atmospheric transport and deposition for the given cluster. It was believed that in doing so, potential biases from choosing two days with nearly identical deposition patterns would be minimized.

Table 8.
Representative Cluster Days Chosen for Hybrid Modeling Exercise

Cluster Number	Wet Days	Dry Days
1	29 MAY 1996 09 SEP 1995	22 FEB 1996 27 JUN 1995
2	13 MAY 1996 16 AUG 1995	20 SEP 1995 06 JUN 1996
3	11 SEP 1995 13 JUN 1996	17 DEC 1995 30 MAR 1996
4	11 MAR 1996 29 SEP 1995	23 OCT 1995 07 FEB 1996
5	19 MAR 1996 09 APR 1996	17 FEB 1996 21 MAR 1996
6	23 JUN 1996 27 MAY 1996	13 APR 1996 07 MAR 1996
7	02 MAR 1996 15 OCT 1995	12 JAN 1996 22 MAY 1996
8	Not Modeled*	03 MAR 1996 23 DEC 1995

* No days with rain (>1mm) occurred during the year of record

4.2.2 Airshed Pollutant Loads

Atmospheric inputs of mercury to WCA 3A-15 were estimated for both wet and dry deposition as described above. The model estimates reported here were developed using the source-specific emissions rates and mercury speciation factors used in the USEPA Mercury Study Report to Congress. Two additional emissions scenarios were evaluated but not used in this analysis, as described in Appendix 1. Results from the dry deposition simulations were used, in conjunction with measured wet deposition rates, as input into E-MCM. Detailed discussions of the atmospheric modeling can be found in Appendix I.

Wet Deposition

These model results predicted a total mercury wet deposition of 18.74 ± 1.57 $\mu g/m^2/yr$. (± 1 standard deviation) to WCA 3A-15. The temporal variation in the wet deposition of total mercury to the WCA 3A-15 is presented in **Figure 6.** As would be expected from the marked seasonality of rainfall in south Florida, the model indicates a significant seasonal trend in total mercury wet deposition to the area, predicting that over 80 percent of the wet deposition would occur from May through October.

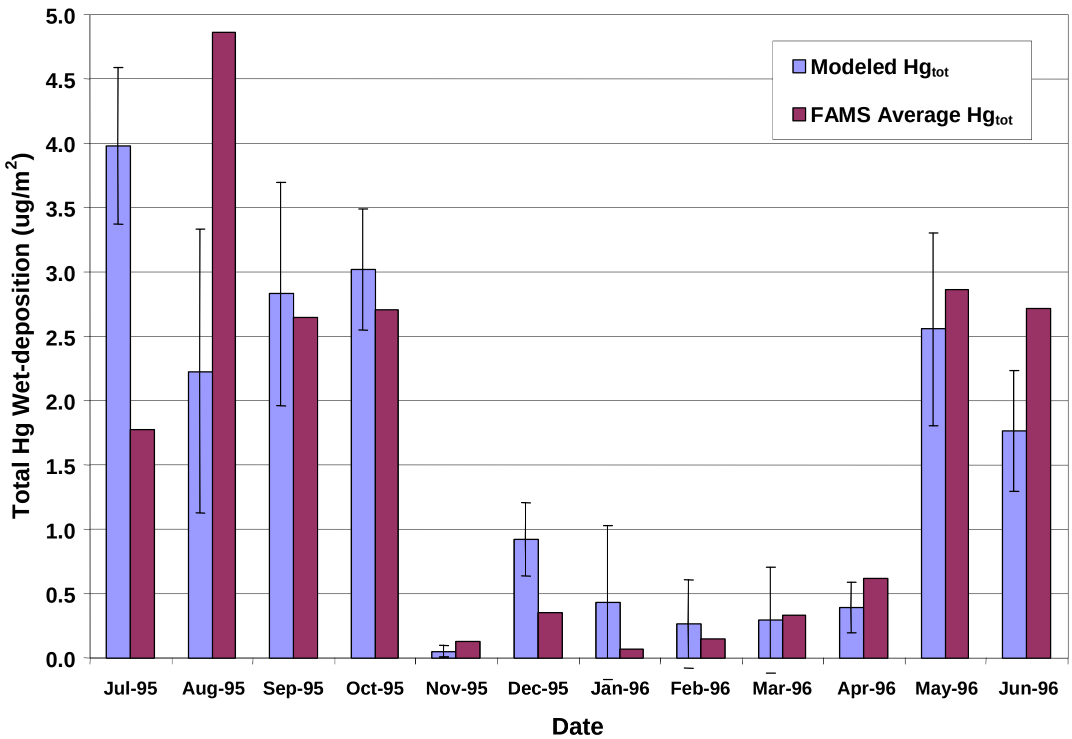

Figure 6. Comparison of the modeled monthly total mercury wet deposition to WCA 3A-15 and FAMS[8] observed total mercury wet deposition (average of Tamiami Trail Ranger Station and Andytown sites).

The speciated mercury wet deposition is presented in **Figure 7**. From this figure, it can be seen that the predicted total wet deposition of mercury is dominated by deposition of reactive gaseous mercury (RGM), believed to be in the form of Hg(II). In contrast, model results suggest that the deposition of gaseous elemental mercury, Hg(0), is negligible. Once again, the seasonal nature of the deposition is apparent.

[8] The Florida Atmospheric Mercury Study (FAMS) measured mercury deposition (both bulk and wet-only rainfall collection), particulate-associated mercury and total gas-phase mercury (TGM) at 9 sites in Florida (i.e. panhandle, north-central Florida, marine background site, 4 sites near the Everglades, and 2 sites in the southwestern peninsula). Long-term integrated samples were collected (monthly precip, weekly TGM and Hg(p). Operations began in 1993; all sites were operational by mid-1995 and operated through the end of 1996 (Pollman, *et al*., 1995; Guentzel, 1997; Guentzel, *et al*., 2001).

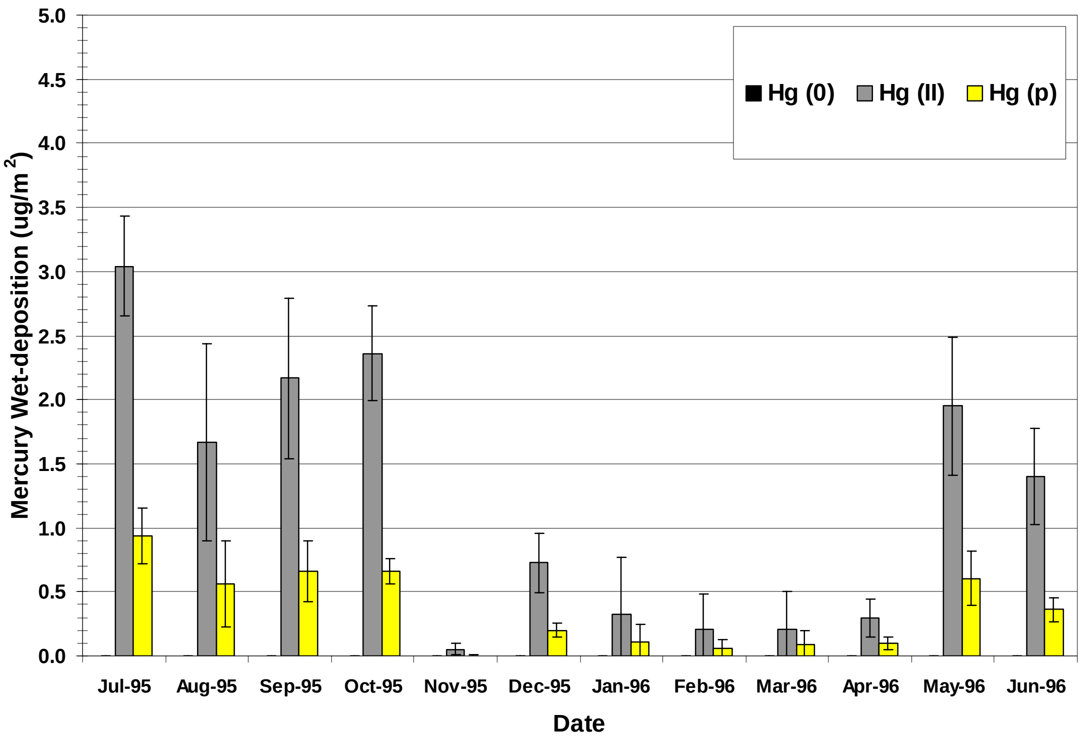

Figure 7. Modeled monthly speciated mercury wet deposition to WCA 3A-15.

Dry Deposition

The hybrid model estimates of the dry deposition of mercury to the WCA 3A-15 were performed for the same emissions inventory employed in the wet deposition modeling (Appendix I). As for the simulated wet deposition results, the results presented here use the emissions from the USEPA Mercury Report to Congress as input for the model.

The hybrid model estimate for dry deposition of mercury to WCA 3A-15 during the one-year period of record was 12.2 ± 2.0 $\mu g/m^2/yr$. (± 1 standard deviation). While considerable variability was evident in the monthly deposition estimates, on average, dry deposition to the site showed a seasonal trend, with relatively greater deposition occurring during the climatological wet season. As was the case for the wet deposition to WCA 3A-15, dry deposition to this area is dominated by the Hg(II) fraction. Note that the dry deposition estimate derives from local source emissions alone and includes no contribution from global background.

Levels of Hg(II) calculated by the model were the result of the dispersion and deposition of Hg(II) emissions from the USEPA Mercury Study Report to Congress (USEPA, 1997), not the result of Hg(II) production from atmospheric chemical reactions. Measurements of Hg(II) species in the atmosphere were not available due to the limitations of measurement techniques. In addition, based on our understanding of the rates of conversion of Hg(0) to Hg(II) at the time, the conversion of Hg(0) to RGM during passage from the coast to the Everglades was too slow to be significant, and therefore not included in these calculations.

By 1999 more robust techniques had been developed and field measurements were available for comparison with model results. Interestingly, the levels of Hg(II) predicted by the model were consistent with the values measured by the UMAQL and USEPA FEDDS and SAMPEX studies in south Florida during 1998 and 2000. Values of Hg(II) were measured and estimated by the model to range from 0 to 100 pg/m^3 and varied spatially and temporally across the eastern portion of the Everglades in Broward County.

Model-calculated total atmospheric deposition of mercury to WCA 3A, estimated as the sum of the wet and dry deposition, is approximately 30.94 ± 13.55.

One end point of the atmospheric modeling was selection of the appropriate loading term of mercury to the 3A-15 study site. While we had both measured and modeled wet deposition rate estimates, we chose a combination of measured wet deposition of 23.1 $\mu g/m^2$/yr. from the FAMS project (average of deposition rates for the Andytown, Fakahatchee Strand and Tamiami Trail sites) and the modeled estimate of dry deposition 12.2 ± 2.0 $\mu g/m^2$/yr., for a total of 35 $\mu g/m^2$/yr. For all ensuing aquatic cycling modeling efforts, this combined estimate was used.

4.3 Aquatic Mercury Cycling Modeling

A dynamic mercury cycling model has been developed to simulate the conditions found in marsh areas of the Florida Everglades. The Everglades Mercury Cycling Model (E-MCM) (Tetra Tech, 1999b) is an adaptation of the Dynamic Mercury Cycling Model for lakes (D-MCM) (Tetra Tech, 1996, 1999a). E-MCM accommodates unique features of Everglades marshes from the point of view of mercury cycling in aquatic systems. These features include shallow waters, a system of canals and managed water levels, a warm subtropical climate, high sun exposure, neutral to alkaline pH, high concentrations of dissolved organic carbon and sulfate, large biomass of aquatic vegetation including periphyton, sawgrass, cattails and water lilies, and a wide range of nutrient levels and primary productivity. Field data (USEPA, 1998) for parts of the Everglades have shown considerable spatial and temporal variability, with some locations apparently conducive to methylmercury production and bioaccumulation.

E-MCM also incorporates recent advances made by researchers investigating mercury cycling in freshwater systems and in the Everglades specifically. These advances include an improved understanding of the factors governing methylation, demethylation, Hg(II) reduction, food web mercury transfers, and the role of aquatic vegetation in the mercury cycle (e.g. Krabbenhoft, *et al.*, 1998, Gilmour, *et al.*, 1998a, Hurley, *et al.*, 1998, Cleckner, *et al.*, 1998).

4.3.1 Model Description

E-MCM is a mechanistic simulation model that runs on Windows™-based computers. The model uses a mass balance approach to predict time-dependent concentrations of the three primary forms of mercury [methylmercury, Hg(II), and elemental mercury (Hg(0)] in water and sediments (dissolved and particulate phases), vegetation, and a simplified food web (**Figure 8**).

Model compartments include the water column, three macrophyte species (cattails, sawgrass, water lilies), up to four sediment layers and a food web. The model has two types of particles in the water column: detritus and "other" suspended solids, plus solids in the sediments. For each type of particles - detrital, suspended and sediment solids - compartments have been set up for two types of Hg(II) exchange: (1) instantaneous and (2) slow exchange governed by the kinetics of adsorption and desorption.

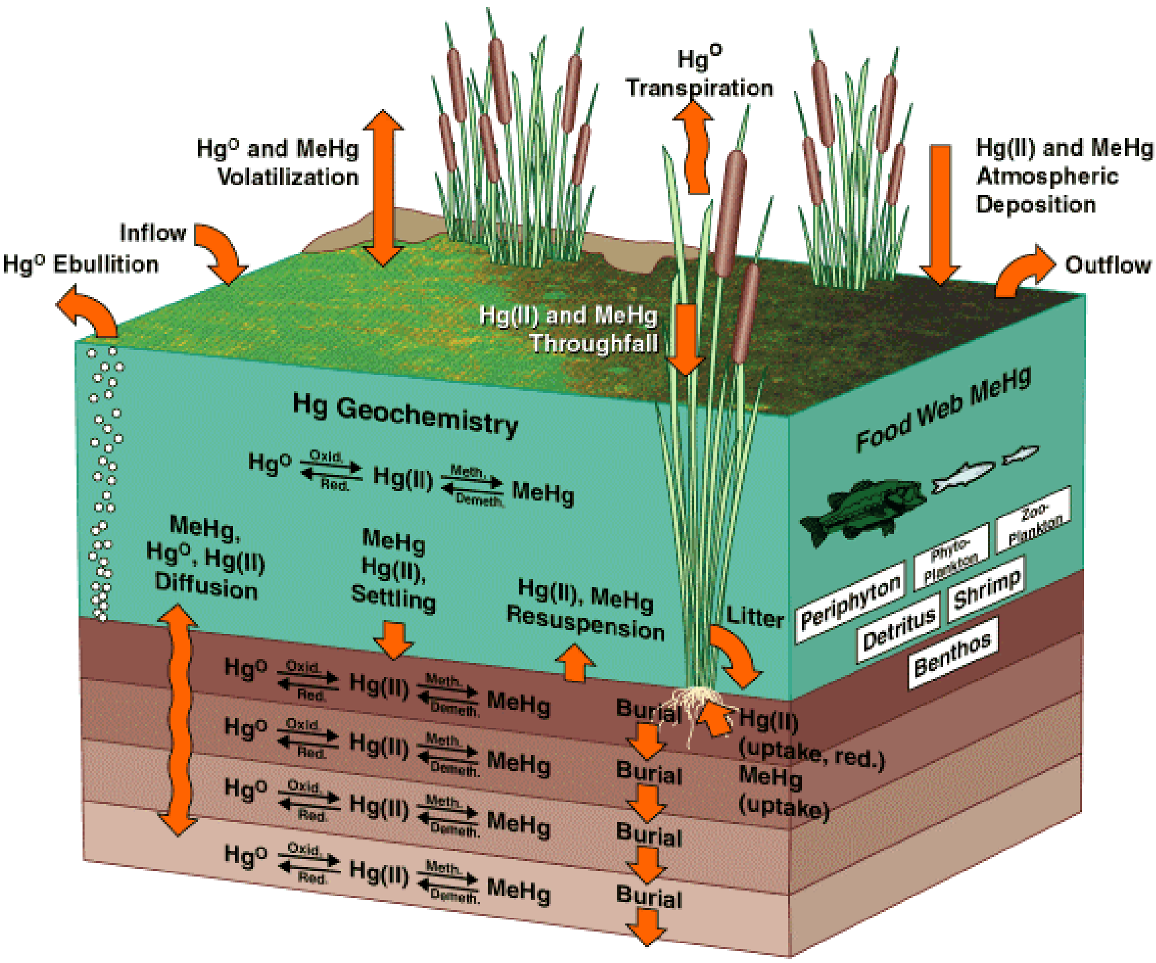

Figure 8. Conceptual model of aquatic mercury cycling processes described in the Everglades Mercury Cycling Model (E-MCM).

The simplified food web consists of detritus, periphyton, phytoplankton, zooplankton, benthos, shrimp, *Gambusia* (mosquitofish), bluegill/warmouth sunfish, and largemouth bass. Fish mercury concentrations tend to increase with fish age, and are therefore followed in each year-class (up to 20 cohorts for each species). Bioenergetics equations developed for individual fish at the University of Wisconsin (Hewett and Johnson, 1992) are modified to consider temperature dependent growth and coupled to methylmercury fluxes (Harris and Bodaly, 1998). These fluxes for individual fish are then adapted to simulate year classes and entire populations (Tetra Tech, 1999b).

Major processes involved in the mercury cycle in an Everglades marsh are shown in **Figure 8**. These processes include surface inflows and outflows, vertical groundwater flow, instantaneous mercury partitioning between some binding sites on abiotic solids and dissolved complexes, slower adsorption/desorption kinetics for Hg(II) on other sites on abiotic solids (see Appendix A, Modeled Deposition of Mercury to Everglades Water Conservation Area 3A-15), particulate settling, resuspension and burial, macrophyte related fluxes (throughfall, litter, transpiration), atmospheric deposition, air/water gaseous exchange, *in-situ* transformations (e.g. methylation, demethylation, methylmercury photodegradation, Hg(II) reduction, Hg(0) oxidation), mercury kinetics in plankton, and methylmercury fluxes in fish populations (uptake via food and water, excretion, egestion, mortality, fishing).

Although the Everglades is shallow, significant temperature vertical gradients in the water column have been observed by ACME researchers (D. Krabbenhoft, unpublished data). The model allows for surface and bottom water layer compartments if desired.

4.3.2 Modeling Approach

The aquatic mercury cycling component of this project uses the site designated as WCA 3A-15 as the basis for the model calibration and calculations. Site WCA 3A-15 is in the northern portion of WCA 3A and was selected because it has elevated mercury concentrations in largemouth bass, and has been extensively studied by the USGS ACME program. The approach to aquatic modeling for the pilot mercury TMDL included the following key components:

- Calibration of E-MCM using estimates of typical long-term conditions at site WCA 3A-15 (e.g. after 100 years. of simulation). The critical endpoint was mercury in largemouth bass, but the calibration examined total and methylmercury concentrations in each compartment for which data were available. The model calibration was performed using average wet deposition rates measured by the FAMS program between 1993 and 1996 at the FAMS sites located at Tamiami Trail, Fakahatchee Strand, and Beard Research Center in Everglades National Park (Guentzel, 1997; Guentzel, *et al.*, 2001; see Appendix II, Section 4.3). Dry deposition rates were obtained from the hybrid modeling conducted by UMAQL.

- Development of a long term steady- state dose-response curve relating predicted long-term average fish mercury concentrations to different levels of long term continuous atmospheric Hg(II) deposition. For example, if atmospheric deposition decreased to 50% of current levels and was maintained at the lower value for a long period, at what concentration would mercury in fish ultimately stabilize? Model runs were carried out for several mercury deposition scenarios to develop the curve.

- Assessment of the predicted timing of the response of fish mercury concentrations to different loadings of inorganic Hg(II).
- Sensitivity analysis of E-MCM predictions to various model input parameters, including atmospheric deposition rates of mercury.
- Assessment of the effects of year-to-year variations of atmospheric deposition under long-term constant mean annual loadings.
- Uncertainty analysis: Quantifying the effects of uncertainty regarding true current atmospheric deposition rates on model predictions and study conclusions.

General characteristics of site WCA 3A-15 are summarized in **Table 9**.

Table 9.
Characteristics of Water Conservation Area 3A-15

Parameter	Value
Area modeled	1 km x 1 km
Surface water depth	0.2 to 0.7 m
Air temperatures (monthly means)	12 to 30 C
Productivity	Low to Moderate
Flow pattern	Surface flow
Stratification	Intermittent
Anoxia	Yes
Dissolved organic carbon	~ 16 mg/L
Surface water pH	~ 7.2
Surface water chloride	~ 5 mg/L
Surface water sulfate	100 μeq/L
Sedimentation rate	< 1 cm/yr.
TSS	~ 2 mg/L
Macrophytes	Includes sawgrass, cattails, water lilies
Fraction of marsh with open water	<50%
Periphyton density	dense

Top predator fish	Largemouth bass

An important note on the model calibration is that, under ideal circumstances, E-MCM would have been calibrated to a long-term data set. Unfortunately, such long-term water chemistry and biota data sets do not exist, nor do high-quality, high-resolution mercury deposition and sediment accumulation rate data. This currently precludes a long-term, historical calibration, and was the impetus for choosing a calibration approach that assumed that current conditions reflect long-term dynamics – in essence, a quasi steady-state calibration. Further information on the approach to model calibration, sensitivity analysis, uncertainty analysis and assessment of year-to-year variations are provided below and discussed in detail in Appendix II.

Model Inputs

In response to the mercury issue in the Everglades, several agencies initiated research and monitoring programs in the 1990's as the SFMSP. These began with the FAMS and USEPA Regional Environmental Monitoring and Assessment Program (REMAP) project. In 1993-1995 REMAP collected extensive data on the canal system, and in 1995-1996 sampled water, soil, vegetation and fish at 500 sites. Subsequently, in 1999, REMAP again sampled across the entire marsh system, examining the relationships between parameters and temporal trends. A joint study by USEPA and SFWMD sampled 9 surface water control structures over two years. (1993-1995) to determine surface water loads to the Everglades Protection Area (**Table 1**). FWC collects and maintains a long-term database on mercury in largemouth bass and other fishes. As a result, there are extensive air, water, soils and biota data on mercury at WCA 3A-15. From 1995 through the present, the USGS ACME Team has conducted intensive process-oriented research at 9 sites from north to south in the Everglades. Data from all these studies have been used to guide formulation and parameterization of the Everglades-Mercury Cycling Model, and subsequently its testing under a variety of Everglades conditions.

Estimates of atmospheric loading rates of mercury via wet deposition are available from three sources:

1. Direct estimates of wet deposition for three sites in the Everglades region obtained as part of the FAMS monitoring program conducted between 1992 and 1996;
2. Direct estimates of wet deposition for three MDN sites in the Everglades region between late 1995 and the present, and
3. Modeled estimates of wet deposition derived from the source-receptor modeling conducted by UMAQL as part of this study.

Dry deposition fluxes are difficult to measure directly with reasonable precision, and are usually inferred in part from modeling. Carefully conducted direct measurements of wet deposition such as those obtained during FAMS are inarguably more reliable than estimates derived from source receptor modeling. For that reason, we elected to use the wet deposition fluxes directly measured during FAMS as input to E-MCM.[9]

Input data types and sources for WCA 3A-15 long-term simulations are summarized in **Table 10**. Mercury concentrations from the atmospheric model were input as boundary conditions to calculate fluxes across the air/water interface (gaseous, wet deposition, dry deposition, deposition of reactive gaseous mercury). Additional information describing inputs used in simulations is provided in Appendix II.

Table 10. Summary of Data Inputs by Major Data Type Category

Data Type	**Parameter Estimate and Source**
Hydrologic Data	
Precipitation	Monthly means from FAMS sites AT, FS, and TT, 1992-1996 (Guentzel, '97; Gill, *et al.*, '99)
Surface water elevations	Direct daily measurements (USGS, Miami Florida Sub District Office)
Surface Flow	Monthly means computed based on cell size configuration, assumed hydraulic retention time, and precipitation seasonality.
Physical Data	
Temperature and incident light	Monthly means estimated from NOAA gauge data at West Palm Beach, 10/89 to 9/94 – HydroQual (1997)
Soil moisture content	Assumed 100% saturation at all times
Mercury Loadings	
Wet Hg(II) deposition	Monthly means from FAMS sites AT, FS, and TT, 1992 –1996. Guentzel, 1997; Gill, *et al.*, 1999.
Dry Hg(II) deposition	Model mean monthly estimates from Keeler, *et al.*, (2001)
Leaf Area Index	3 (assumed)
Upstream Surface water concentrations – Hg(II)	Based on average for 3A-33 = 2.14 ng/L (n = 7) sampled by USGS
Upstream Surface water concentrations – MeHg (unfiltered)	Based on average for 3A-33 = 0.27 ng/L (n = 7) sampled by USGS

[9] This is not to say that the modeled wet deposition fluxes have little or no value. First, the robustness of the simulated dry deposition fluxes that the E-MCM model relies upon as additional atmospheric input is reflected in part by how well the source-receptor modeling captures the relationship between sources and wet deposition. The extent that the modeled wet deposition fluxes match observed values (*cf.*, Figure 6) provides some assurance that the modeled wet, and by extension, dry deposition relationships are reasonable. Second, the fact that a TMDL analysis requires quantifying the relationship between sources and the target metric also necessitates the modeling of the relationship between sources and wet deposition of mercury.

Surface Water Chemistry	
DOC	ACME data (n = 8) (G. Aiken, USGS unpublished data)
pH and dissolved oxygen	Limno-Tech (1996)
SO_4^{2-}	~100 µeq/L (Gilmour, *et al.*, 1998b)
Hg Concentrations in Marsh	
Surface water Hg_{tot} and MeHg (filtered and unfiltered)	1995-1998 data from ACME (D. Krabbenhoft, unpublished data)
Elemental Hg (DGM)	20 – 40 pg/L (Krabbenhoft, *et al.*, 1998)
Sediment Hg	Gilmour, *et al.*, 1998b
Sediment porewater chemistry	Gilmour, *et al.*, 1998b
Food Web and Vegetation	
Fish growth (largemouth bass) and Hg concentrations	T. Lange, Florida Fish and Wildlife Conservation Commission (unpublished data)
Mosquitofish Hg concentrations	D. Krabbenhoft (ACME unpublished data)
Fish diets	Cleckner and Gorski (ACME unpublished data)
Fish biomasses	Marsh-wide average = 40 kg/ha (wet) (Jordan, 1996 cited in Ambrose, *et al.*, 1997)
Macrophyte and periphyton biomasses and turnover rates	Ambrose *et al.*, 1997
Macrophyte Hg_{tot} concentrations	USGS collected samples, DEP funded analyses by Frontier Geosciences
Shrimp and zooplankton MeHg concentrations	100 - 200 ng/g (dry) (Cleckner, personal communication)
Benthos MeHg and Hg_{tot} concentrations	No data
Periphyton MeHg and Hg_{tot} concentrations	(Cleckner, *et al.*, 1998)
Particle Dynamics	
Hg(II) Sorption	Calibrated
Sediment accumulation rates	Derived from Delfino, *et al.*, (1993 and 1994)
Sediment decomposition rates	Derived from litter turnover rates and net mass sedimentation.

4.3.3 Linkage of Mercury Loads to Fish Tissue Concentrations

A fundamental question to examine in this pilot TMDL study was the relationship between atmospheric Hg(II) deposition and long term fish mercury concentrations. Once the model was calibrated to the current atmospheric Hg(II) deposition estimate of 35 $\mu g/m^2/yr.$, simulations were also carried out with loadings at 75, 50, 25 and 15% of current levels. In these simulations, Hg(II) and methylmercury concentrations in inflows were adjusted in proportion to Hg(II) deposition. Atmospheric loadings of methylmercury also were changed proportionally. Predicted fish mercury concentrations were compared after each simulation had run 200 years, producing essentially steady state conditions. Annual cycles of site conditions and mercury deposition were repeated throughout the simulation period.

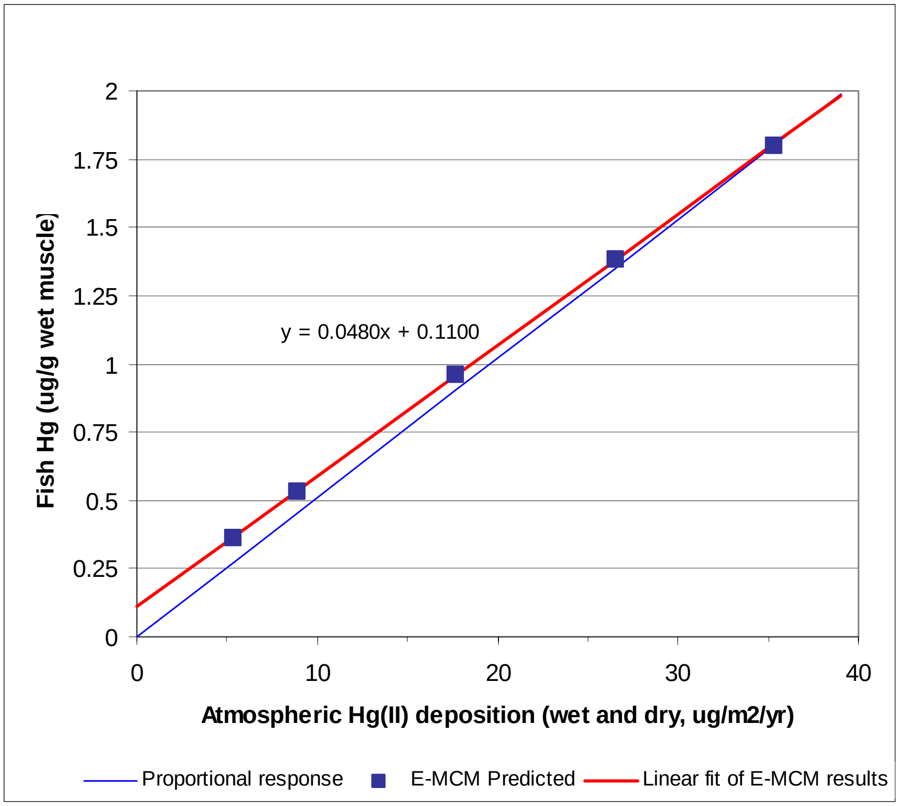

Figure 9. Predicted Hg concentrations in age 3 largemouth bass as a function of different long term constant annual rates of wet and dry Hg(II) deposition. Predictions are based on calibration to current loading of 31 $\mu g/m^2/yr$.

Figure 9 shows the predicted long term relationship between atmospheric mercury deposition and mercury concentrations in age 3 largemouth bass in WCA 3A-15. A linear relationship is predicted, but the slope is not 1.0 and the intercept is non-zero. This suggests that there is not an exact correspondence between relative reductions in Hg(II) loading and fish mercury response. Moreover, the figure suggests that, in the absence of any Hg(II) loading, there will still be some mercury accumulating in largemouth bass. The source of this mercury is, in essence, "legacy" mercury, historically deposited and now lying deep within the sediments (5 to 20 cm below the sediment-water interface) that the model predicts is mobilized and brought into the water column by macrophyte roots. As **Figure 9** illustrates, this source of mercury becomes important only if atmospheric sources are substantially reduced. Eventually this legacy mercury would become exhausted, but at current sedimentation rates, the model predicts that this would not occur for some hundreds of years.

Both the linearity and the deviation of the predicted relationship from unity are strongly influenced by model assumptions not verified by field data. These include:

1. We assumed that two limiting factors govern methylation and demethylation rates: the supply of available mercury and the rate of activity of the methylating and demethylating microbes. We also assumed that methylation occurred in sediments and that it was porewater Hg(II) or a fraction of it being methylated. We further assumed that no cinnabar (HgS) formation would occur for any of the loading scenarios tested. It is possible that cinnabar formation or other geochemical constraints could result in the current levels of porewater Hg(II) remaining unchanged over a range of Hg(II) loading conditions. In this case, methylation rates in sediments might not respond in a linear manner to a change in Hg(II) loading. Work is needed to clarify the location of methylation and demethylation in the system and whether the concentrations of mercury available for the reactions change in response in a linear way to different Hg(II) loading to the system. Stable isotope addition studies conducted by the ACME team using enclosures in the Everglades are expected to yield considerable insight towards these issues. These experiments, which are supported by USGS and DEP, are currently underway.

2. We also assumed that microbial methylation and demethylation rates were limited only by their respective mercury substrates. It is possible that at some point these reactions could be limited by other factors such as the availability of carbon or a micronutrient in short supply.

3. We assumed that Hg(II) and MeHg concentrations in inflows would respond linearly to changes in atmospheric deposition. In fact, if other factors emerge which suggest that Hg(II) or MeHg concentrations in surface waters of the cell being modeled do not respond linearly to changes in atmospheric Hg(II) deposition, then the assumed linear relationship for inflowing mercury would not be appropriate either. This would further contribute to a non-linear response in the cell being modeled.

A second fundamental question addressed by the pilot mercury TMDL was: How fast will fish mercury concentrations change following reductions in mercury loading? This question was examined by running simulations for 200 years to reach steady state conditions, then instantaneously reducing atmospheric deposition as a step function and continuing the simulation for an additional 200 years. Surface water inflowing Hg(II) and MeHg concentrations were reduced as well but, unlike the reductions in atmospheric loading rates, a time lag was imposed on the inflows to reflect the time expected for upstream areas to respond to load changes (see Appendix II, Section 6.3). The results for load reductions of 25, 50, 75 and 85% from the current deposition estimate of 35 $\mu g/m^2/yr$. are shown in **Figure 10**.

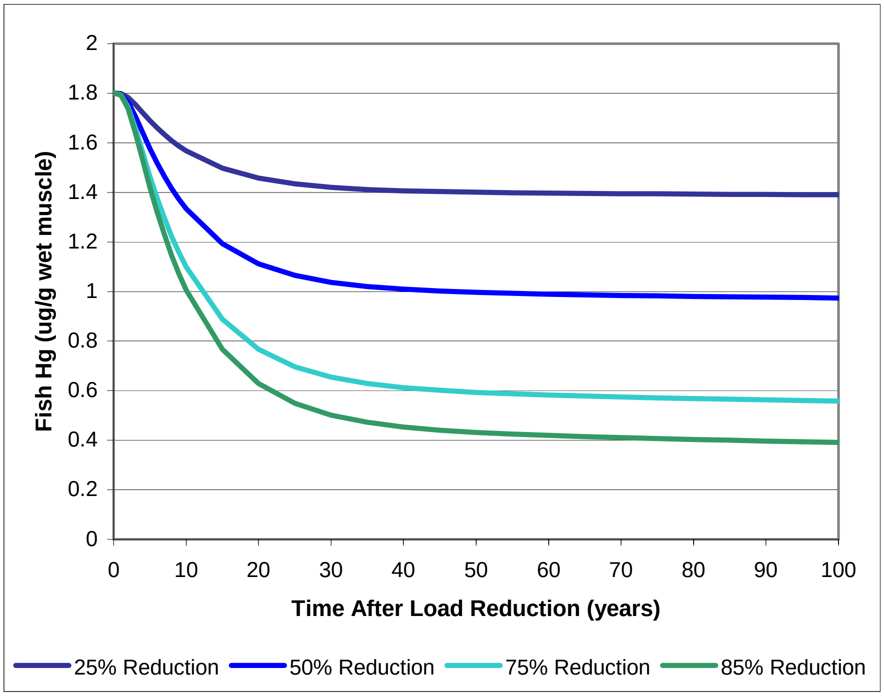

Figure 10. Predicted dynamic response of Hg concentrations in largemouth bass in WCA 3A-15 following different reductions in Hg(II) deposition. Predictions are based on calibration to current loading of 35 $\mu g/m^2/yr$.

Figure 11 shows that the number of years required for the system to approach a new steady state is effectively independent of the actual magnitude of the change. Two phases are illustrated by the curve: the first is a period of comparatively rapid response driven by the decline of Hg(II) loading and the hydraulic residence time of the system; the second phase is far slower, and is governed by the turnover rate of labile Hg(II) in the sediments supporting methylation. Because the simulated concentrations of mercury in largemouth bass ultimately reflect net methylation rates in the sediments, the response of largemouth bass is prolonged. For example, the time required to achieve 50 percent of the ultimate response in fish tissue mercury concentrations is approximately 10 years for all load reduction scenarios tested with the base calibration with atmospheric Hg(II) deposition = 35 $\mu g/m^2/yr$. Within 30 years, approximately 90 percent of the ultimate predicted response is projected to occur.

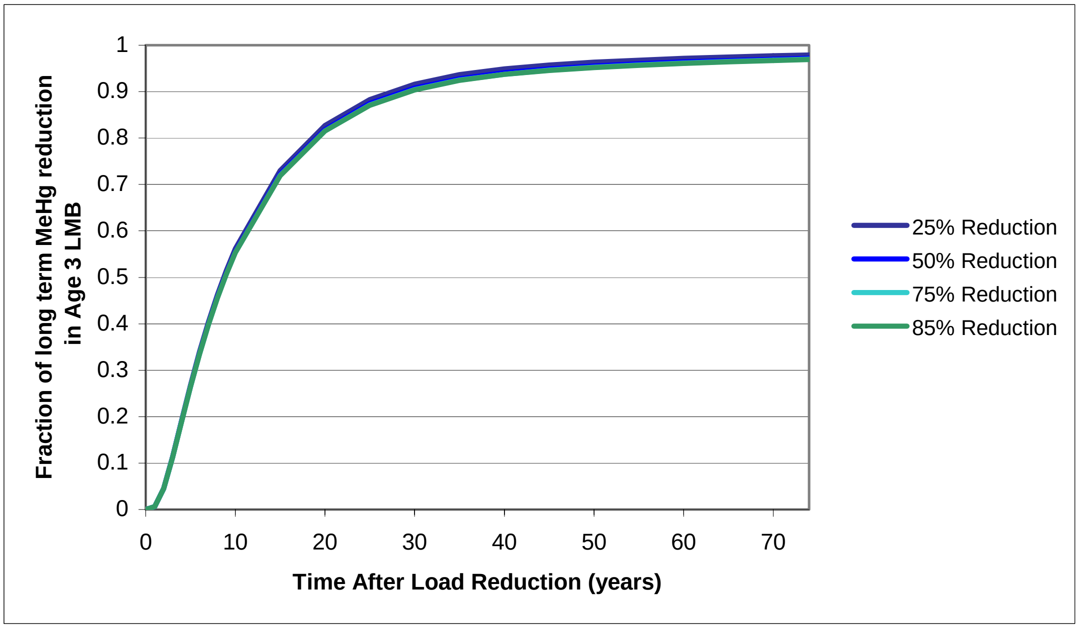

Figure 11. Comparison of the rate at which age 3 largemouth bass concentrations approach steady state following different reductions in Hg(II) deposition (simulations all based on calibration with current Hg(II) deposition = 35 µg/m^2/yr.).

5 UNCERTAINTY ANALYSIS

Assumptions – The limits of our knowledge

Our understanding of the biogeochemical cycle of mercury has advanced greatly in the past decade but a number of features of that cycle remain obscure. In any modeling analysis such as this, the degree of realism in the simulations and the ability of the models to reliably predict future reality (i.e., response to changes or management actions) is based on the degree to which the fundamental processes involved are properly represented in the models. Where these processes are not well understood or can only be represented by empirical data, the results therefrom grow in uncertainty. Several areas where this analysis outpaces the desired level of scientific understanding are discussed below.

5.1.1 The Atmospheric Cycle of Mercury:

The general features of the atmospheric portion of the mercury cycle have been understood for some decades. However, it is only more recently that the importance of speciation as it controls the transport and deposition of mercury has been appreciated. Since 1998 sampling methods have been developed and tested that can measure the relevant gaseous and particulate forms of mercury in both emissions and in the free atmosphere with greater precision and less bias than previously. The key unknowns at this time are the chemical and physical transformations that occur in the atmosphere. Several attempts have been made at construction of global mercury models but all lack key information on the atmospheric reactions of mercury and their rates.

As demonstrated in this analysis, we have achieved a measure of sophistication in measuring and modeling the local transport of emissions, but we lack the context of the overarching global cycle against which to compare local mercury emissions. For example, there is almost no information on ambient concentrations of reactive gaseous mercury in the troposphere, and likely fluxes of reactive gaseous mercury originating from local and hemispheric sources. Yet, it is this chemical species that largely governs wet and dry deposition rates.

The relationship between local emissions and deposition also is very sensitive to our assumptions regarding emission rates and the speciation of emissions**.** Speciated measurements from three different source types in south Florida performed during SoFAMMS (Dvonch, *et al.*, 1999) evinced large (4 to 10x) differences from the emissions inventory compiled by USEPA for south Florida as part of it's 1997 Mercury Study Report to Congress (MSRTC). Subsequent evaluation of the mercury emissions for south Florida, supported by Florida DEP, found similar emissions (within 20% for the large point sources) to those reported in the MSRTC. The speciation results from SoFAMMS clearly indicated that the fraction of reactive gaseous mercury leaving municipal and medical waste incineration facilities was higher than the USEPA inventory reported. The sensitivity of all atmospheric deposition model estimates to the speciation of mercury emitted, and in the ambient air, is currently the greatest source of error. This uncertainty ultimately speaks to our ability to mitigate the problem of high mercury concentrations in fish in the Everglades by controlling local sources. Clearly, the need remains for more substantial and fundamental research on: (1) the nature and magnitude of emissions in south Florida; (2) the magnitude of sources beyond south Florida; and (3) the atmospheric reactions of mercury and their rates.

5.1.2 The Aquatic Cycling of Mercury:

There are many assumptions and parametric uncertainties in the E-MCM. To produce accurate fish mercury concentrations, the model must be calibrated with the actual atmospheric load, including global background. Nevertheless, error analysis shows that this model predicts equivalence between the percent decrease in atmospheric deposition rate and the percent decrease in largemouth bass mercury concentration over the likely range for current estimates of atmospheric deposition of mercury.

5.1.3 Mercury Bioaccumulation and Risk:

The prey fish mercury concentrations that will protect wildlife populations are not accurately known at this time. However, the means of measuring these values are well understood and it is only a matter of finding the resources to carry out these studies.

5.2 Uncertainty

In a complex scientific endeavor, explicit, detailed treatment of the uncertainties inherent in any program of measurement, modeling or analysis is a part of the scientist's duty to be self critical of one's own analyses. Uncertainty is an attribute of all measurements – sampling, analytical, *etc.* – and, in a complex analytical and modeling paradigm, uncertainties may add or compound at each step. It is axiomatic in science that the data must support the conclusions; uncertainty analysis is a requisite for understanding how confident one may be in any particular conclusion.

One goal of this TMDL Pilot Study is to take the present state of the art of mercury research – as exemplified by the SFMSP – and attempt a comprehensive, multimedia integrated analysis. The treatment of the uncertainties herein will give us an indication of the power of our present knowledge and, more constructively, guidance for the final phase of SFMSP studies to constrain these uncertainties to acceptable levels.

5.2.1 The Aquatic Cycling of Mercury

Although considerable research on mercury cycling in aquatic systems is embodied in the E-MCM, several gaps regarding model inputs and the state of knowledge became apparent during the pilot TMDL study which impose uncertainty in the aquatic modeling results. The following recommendations would reduce uncertainty in future model applications:

1. The processes of methylation and demethylation and their rates require further research to improve our understanding and ability to more reliably characterize them. In particular, the environmental factors governing both these processes need to be better understood. For example, the link between sulfur cycling and methylation/demethylation needs to be clarified, including the roles of sulfate reduction and sulfide concentrations. Likewise, the role of periphyton in methylation and demethylation needs to be clarified, including the effects of different periphyton types. The end product of biological demethylation should be elucidated, i.e. (Hg(0) vs. Hg(II)).

2. The sorptive (both adsorption and desorption) characteristics of Hg(II) and MeHg on sediment solids need to be better understood. Sorption helps dictate the amount of Hg(II) in solution and available for methylation; it also has implications regarding response times of the system to changes in atmospheric loading rates of mercury. There are currently experiments underway using stable mercury isotopes to address this issue for a site in the Experimental Lakes Area, Ontario. Similar experimental work is in progress using substrates from the Everglades.

3. Mercury fluxes associated with macrophytes, water column solids, and sediment solids appear to play an important role in mercury cycling in the Everglades. Mercury concentrations in macrophytes (Hg_{tot} and MeHg) should be better quantified, as should the mercury fluxes associated with litter, throughfall, and transpiration. In the current model representation of mercury cycling in macrophytes, we assumed accumulation of RGM and dry particle mercury deposition onto leaves, but did not include any uptake of Hg(II), MeHg, or elemental mercury from the atmosphere directly *into* the plant material. Better information is needed on the sources of mercury accumulated by macrophytes to test this assumption. Furthermore, our approach to Hg(II) uptake by macrophytes suggests that porewater uptake of mercury is incapable of sustaining the high rates of mercury evasion over macrophytes reported by Lindberg, *et al.* (1998). Measurements should be made to confirm the reported flux rates, and research is needed to explain the source of this mercury, i.e. whether it is atmospheric in origin or from the sediments. Clarification also is needed regarding the depths from which most water is drawn into macrophytes and the potential for mercury in deeper sediments to be remobilized via root uptake.

4. We do not have species-specific bioenergetics and growth data for *Gambusia*. This information should be obtained from the literature if available. If such information is not available, experimental work is needed to obtain it.

5. As discussed in the next section, we addressed uncertainty associated with actual Hg(II) deposition rates and year-to-year variability in deposition. We did not address, however, the combined uncertainty and natural variability associated with other

model inputs. A Monte Carlo version of E-MCM has been developed and will be used in future assessments.

6. E-MCM was calibrated assuming site 3A-15 was essentially at steady state relative to current inputs of mercury. As evidenced by recent analyses of both mercury in fish fillets and in wading bird feathers collected in the Everglades – there is a strong indication that declines in the mercury burden for both types of biota have occurred since *ca*. 1990 — this steady-state assumption is in all likelihood incorrect. Ideally, the model calibration would have been time-dependent, and would be able to reproduce historical trends of mercury accumulation in the sediments. Such a calibration relies on independent estimates of the trends in emissions and deposition over approximately the past 100 years that are not available.
7. Finally, we calibrated E-MCM to a single site in this study. We were therefore unable to compare model predictions to observations in terms of the effects of different site conditions such as pH, DOC, fish growth rates, sulfate and sulfide levels, and other site conditions that vary systematically across the Everglades. As part of continuing E-MCM modeling support work funded by DEP and SFWMD, the model is currently being applied to at least five other sites located widely across the Everglades. This will allow testing of the predicted effects of changing site conditions.

5.3 Margin of Safety

A *Margin of Safety* determination is a requisite component of a TMDL analysis to account for the uncertainty in the understanding of the relationship between pollutant loadings and water quality impacts. Typically, this is incorporated explicitly by setting aside a fraction of the calculated maximum acceptable load as an unallocated source, or incorporated implicitly by utilizing a set of appropriately conservative (protective) assumptions in the analysis.

For this analysis, the Margin of Safety can be separated into three components: (1) that associated with the Florida Health Department consumption advisory level of 0.5 mg/kg mercury in fish; (2) that associated with the modeled relationship between atmospheric sources and atmospheric loadings; and (3) that associated with the modeled relationship between loadings and biotic response. To put this pilot effort in context, we describe some aspects of margin of safety that would need to be considered when developing a TMDL involving atmospheric deposition of mercury. These elements are discussed below.

5.3.1 Health risk margin of safety

In light of recent findings, a *Margin of Safety* is not incorporated in the water quality endpoint for this pilot TMDL. That endpoint is the 0.5 mg/kg mercury concentration in fish flesh, fish consumption advisory limit, as issued by the Florida DOH. Concentrations greater than this value trigger the issuance of fish consumption advisories by DOH. This number had been considered protective of human health for exposure to mercury from fish consumption. The 0.5 mg/kg advisory limit was based on the Provisional Tolerable Weekly Intake value proposed by the World Health Organization (WHO) in 1972. However, the mercury reference dose used by the WHO of 0.43 μg/kg body weight-day exceeds the recent USEPA recommended and National Research Council confirmed reference dose of 0.1 μg/kg body weight-day. As well, the Florida relative source contribution for mercury from human consumption of marine and estuarine fish is in need of recalculation based on new data which indicate that fish consumption by Floridians is higher that the national average. This, along with the recent USEPA issuance of a guidance mercury water quality criterion for protection of human health of 0.3 mg/kg mercury concentration in fish flesh, suggests that the Florida 0.5 mg/kg limit is not conservative. The Florida 0.5 mg/kg advisory limit is currently under review.

5.3.2 Atmospheric modeling margin of safety

The manner in which atmospheric sources were considered and used in the source-receptor modeling must be considered *non-conservative* at this juncture. The current state of the art in atmospheric source-receptor modeling used in the analysis does not allow for background sources beyond the immediate model domain to be considered explicitly. Since the model considers only local sources as the forcing function controlling mercury deposition in the Everglades and, since local sources are the only inputs that have a reasonable likelihood of control, this makes the allocation of an acceptable load inherently *non-conservative*. Given that we cannot control background sources, to the extent that mercury fluxes into the Everglades are derived from global or regional sources, the benefit of controls on local sources would be minimized proportionately.

5.3.3 Aquatic cycling model margin of safety

The aquatic cycling modeling does not incorporate any margin of safety explicitly. The model was calibrated to our best estimates of current conditions to try and accurately simulate both existing and likely future behavior of mercury at Site 3A-15. A margin of safety could be incorporated into the analysis that considers the inherent uncertainty in the model predictions, but is not reasonably possible until the Monte Carlo capabilities are completed in E-MCM.

In summary, a margin of safety was initially built into the analysis by virtue of using the Florida Health Department consumption advisory level of 0.5 mg/kg, however the revised USEPA fish methylmercury criterion of 0.3 mg/kg eliminates that margin of safety. Given that controlling global sources is infeasible, however, our inability to resolve the contributions of global and local sources to deposition at Site 3A-15 suggests that we have underestimated the likely requisite local load reduction. When reasonable lower limits of global loadings are considered, our results indicate that virtually complete elimination of local sources is likely required to approach or achieve reductions in mercury concentrations in largemouth bass consistent with achieving a target level of 0.5 mg/kg.

5.4 Sources of Uncertainty

5.4.1 Aquatic Mercury Cycling Model – Conceptual Issues

One element of uncertainty analysis as applied to models is sensitivity analysis, i.e. understanding, in the present case, which variables in the E-MCM most affect predicted fish mercury concentrations at WCA 3A-15. Two types of sensitivity analyses were conducted to address this question. The first approach was to conduct a traditional type of analysis where each parameter is varied by the same relative amount, without regard to whether this value is actually likely to occur or is appropriate for the system of interest. The second approach considered the range of actual or (if such information was not available) likely values a parameter can assume. This latter approach is essentially a "minimum-maximum" analysis that examines sensitivity in the context of likely or actual parameter distributional ranges. It thus defines the bounds of uncertainty in model response related to a given variable. Details of the approaches and a presentation of the input parameter values used in the analyses are presented in Appendix II.

5.4.2 Traditional Sensitivity Analysis Results

Simulations were run varying inputs in isolation by a given amount, for example plus and minus 50%. In cases where a 50% change did not make physical sense, a lesser change was made, e.g. 10% or 25%. In addition, there were some inputs such as the fraction of fish in the diet that did not make sense to change in isolation. The following simultaneous changes were simulated:

- Fish growth rates and spawning sizes for all fish species were changed by the same percentage simultaneously.

- The areal coverage of the three macrophyte species, periphyton coverage, and quantities of suspended solids and detrital material in the water column were varied simultaneously. It is expected that a change in vegetation cover would affect the amount of settling material. Burial rates would be affected by these changes, since burial is calculated based on sources and sinks of particulate matter to the sediments.

- When the diet of largemouth bass was altered to increase or decrease the fraction of fish in the diet, it was necessary to also alter the fractions of the diet represented by other food items. The fractions added or subtracted from fish consumption were distributed evenly amongst other food items.

- Surface inflow and outflow rates (Qin and Qout) were varied simultaneously since it was assumed these rates were equal in simulations. This assumption is reasonable, given that estimated average flows in and out of WCA-3A over a 31-year period agreed within 12% (SFWMD, 2000).

- When atmospheric Hg(II) deposition was altered, surface inflowing Hg(II) and MeHg loads also were varied proportionately. Because the rates of atmospheric methylmercury deposition are so low compared to other major fluxes, atmospheric methylmercury deposition was not altered for this particular analysis.

To provide a common basis for comparing the effects of changes to model inputs on fish mercury, the concentrations in age 3 largemouth bass were used as the endpoint (**Figure 12**). Results are presented as absolute value of the ratio of the percent change in fish mercury concentration divided by the percent change in the input:

Ratio = |Percent change in fish Hg| / |Percent change in input value|

Predicted mercury concentrations in age-3 largemouth bass were most sensitive to factors associated with particle and vegetation fluxes, Hg(II) loading, methylation rates, and factors affecting fish diets and growth.

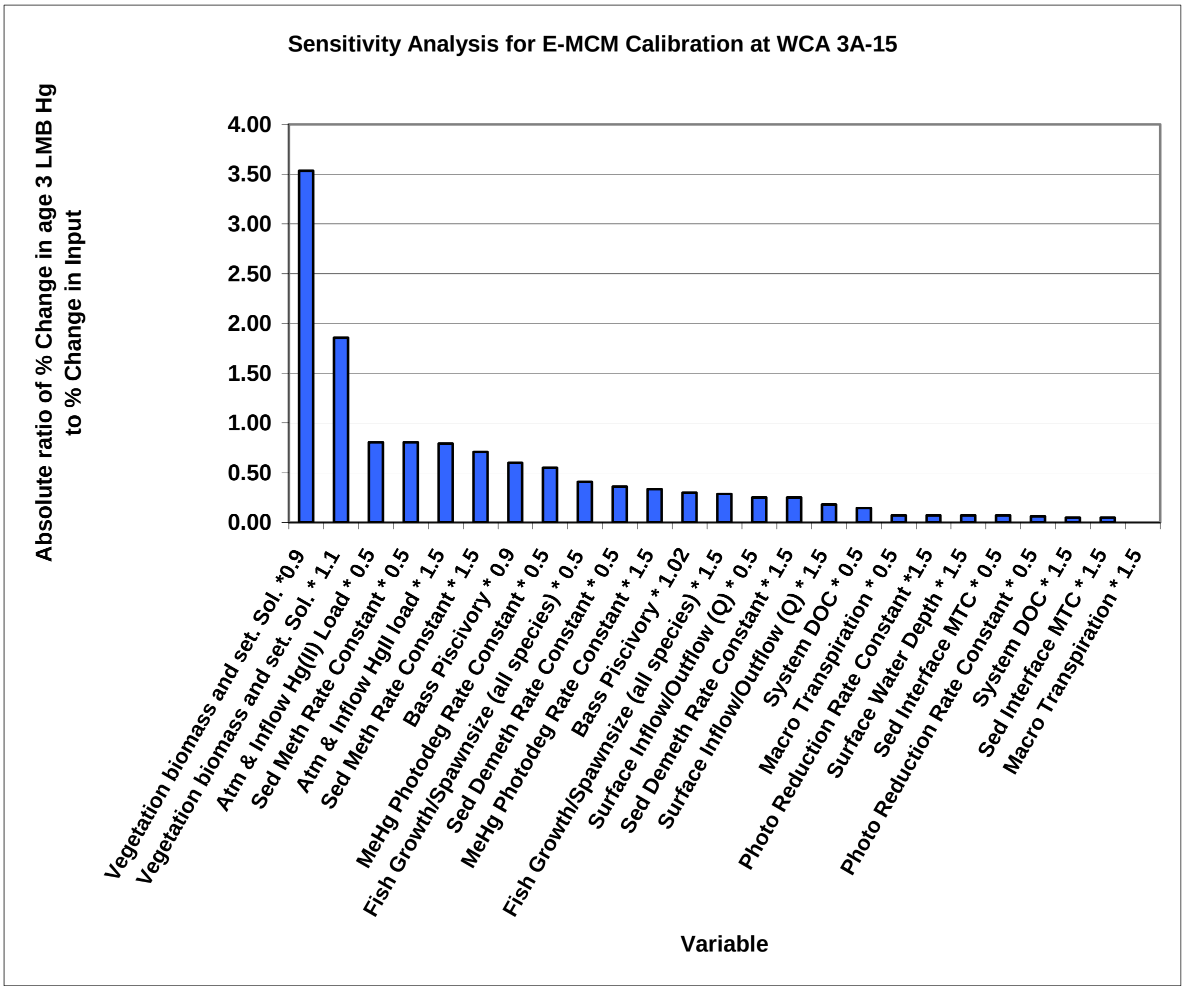

Figure 12. Predicted sensitivity of age 3 largemouth bass mercury concentrations in WCA 3A-15 to changes in various input values.

Another important conceptual issue is whether the relationship between biota response and external mercury loading rates to the system is linear. E-MCM predicts long term responses of fish mercury concentrations to changes in atmospheric Hg(II) deposition rates are virtually linear (but with a non-zero intercept) over practical time scales. The model predictions are governed, and to some extent made uncertain, by our current understanding of mercury cycling and the resulting assumptions in the model. Specifically, the following assumptions had a significant impact on the shape of the dose-response curve:

- Methylation occurs primarily in the sediments;
- Methylation depends on a bioavailable fraction of porewater Hg(II);
- Porewater Hg(II) concentrations are not currently at saturation. For example, it is plausible that additional Hg(II) loading could result in precipitation of the excess Hg(II) as cinnabar, with no change in porewater Hg(II). We do not have cinnabar forming in any of the loading scenarios we examined with our calibration; and
- Atmospheric methylmercury deposition, inflowing methylmercury loads, and inflowing Hg(II) loads were assumed to be reduced by the same percentage as Hg(II) deposition in scenarios with load reductions. In other words, no watershed-based upstream sources, i.e. geologic or anthropogenic, within the watershed are assumed to exist. In effect this means all upstream surface water loadings are derived from atmospheric deposition influenced to the same extent by variations in emissions as direct atmospheric inputs to WCA 3A-15. To put this assumption in perspective, given that atmospheric deposition to the Everglades constitutes >95% of the annual mercury load, the upper bound of watershed based sources is at most only a second order consideration.

Thus, we interpret the predicted response of fish mercury concentrations to load reductions in this study to reflect the current level of understanding. This level of understanding is currently inadequate, however, to support strong confidence in the absolute values of predicted fish mercury levels. Nonetheless, we are relatively confident in our ability to predict the percentage change in fish mercury concentrations from the percentage change in atmospheric loading. We recognize, of course, that the relationship between emissions and atmospheric deposition is dictated by a number of factors, including speciation of emissions and other source characteristics. Thus, while we can state that our analysis indicates that a desired percentage reduction requires a commensurate reduction in atmospheric loadings, the desired percentage change in atmospheric loadings does not necessarily equate to a similar reduction in overall emissions.

5.4.3 "Minimum-Maximum" Sensitivity Analysis Results

To conduct the "minimum-maximum" analysis, E-MCM was first run for the i^{th} parameter at its high and low limits, while all other parameters were held constant at their nominal values. As in the more traditional sensitivity analyses presented earlier, the end-point for the analysis was the MeHg concentration in age 3 largemouth bass. The sensitivity index for the i^{th} parameter (SI_i) (Hoffman and Gardner, 1983) is calculated as:

$$SI_i = 1 - \frac{E_{i,low}}{E_{i,high}}$$

where $E_{i,low}$ and $E_{i,high}$ are the predicted age 3 largemouth bass mercury concentrations for the low and high estimates for the i^{th} parameter respectively. Note that, as SI_i approaches 1 (i.e., the larger the difference between the high and low results), the model is increasingly more sensitive to the range in parameter uncertainty.

Results from the "minimum-maximum" analysis are shown in **Figure 13**. The analysis demonstrated that predicted concentrations of mercury in age 3 largemouth bass at WCA 3A-15 are most sensitive to uncertainties associated with inputs related to the *in situ* production and destruction of methylmercury. This is because: (1) *in situ* methylation is predicted to be a major source of MeHg for fish at WCA 3A-15; and (2) there is considerable uncertainty regarding true rates. This result is consistent with previous assessments indicating that future R&D efforts need to better elucidate factors affecting fish mercury concentrations in Everglades marshes, and aquatic systems in general.

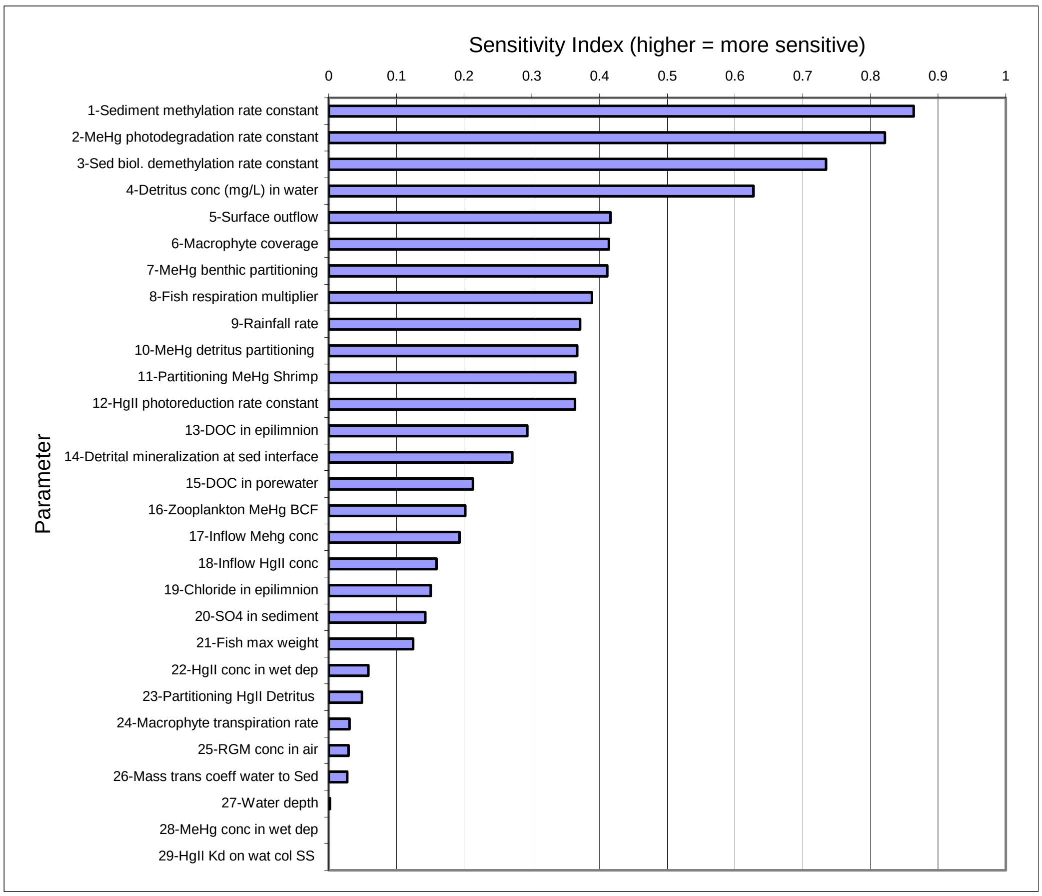

Figure 13. Calculated SI values for different E-MCM model parameters analyzed using the 'minimum-maximum' sensitivity analysis approach.

In addition, uncertainties associated with particle-based mercury fluxes also significantly affected predicted fish mercury levels. There is a need to better constrain/estimate the production and fate of particulate matter via macrophytes and periphyton for the purposes of better constraining E-MCM predictions. Uncertainties regarding hydrologic inputs had a moderate effect on predicted fish mercury concentrations. Because these parameters were altered individually, this result was anticipated and the full impacts of hydrological changes and uncertainties are likely not reflected in this analysis.

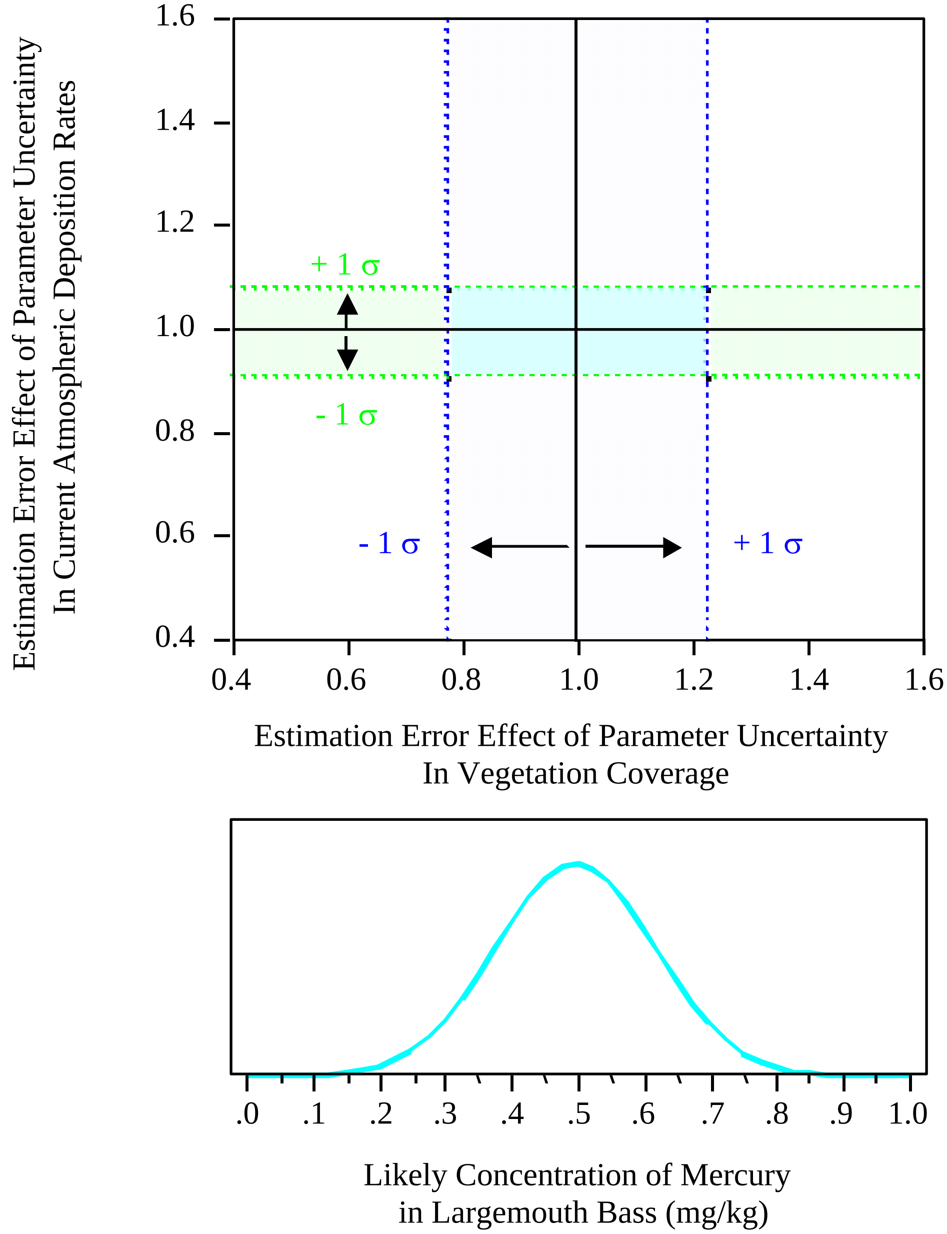

Figure 14. The effects of parameter error on predicted mercury concentrations in largemouth bass (LMB) following a reduction in current atmospheric loading rates by 17.7 μg/m^2/yr. (assumed current rate = 35 μg/m^2/yr.). Analysis assumes that the initial predicted concentration in LMB in the absence of error is 1 mg/kg. See text for explanation.

5.4.4 Effects of Parameter Uncertainty

The sensitivity index approach, as currently used, treated only one parameter at a time. An improvement to this approach would be to simultaneously vary groups of interdependent inputs to their minima or maxima (positive or negatively correlated).

Figure 14 presents an example of Monte Carlo analysis. In this analysis, the estimated uncertainty in modeled atmospheric deposition was combined with the uncertainty of a single parameter set within E-MCM – vegetative cover and settling solids. For the sake of simplicity, the analysis assumes that current largemouth bass concentrations average 1 mg/kg in the absence of error. In the upper panel, the effect of parameter error on LMB concentrations is delineated by reference lines showing the standard deviation of the predicted LMB concentrations. For example, the X-axis shows via dotted lines the relative standard deviation in predicted largemouth bass (LMB) mercury concentrations due to an assumed variability in vegetation turnover rate of 10%. Resultant variability in predicted LMB due to this factor alone is approximately 23%. Likewise, the Y-axis shows the relative standard deviation in predicted LMB mercury concentrations due to errors in the total deposition rate (8.3%).

The effects of the joint error distribution in these two parameters can be readily calculated by assuming the effects of the two errors are multiplicative which, based on model testing, is a reasonable assumption. The resulting uncertainty can then be used to assess the uncertainty in predicted largemouth bass mercury concentrations given a particular atmospheric load reduction. This is illustrated in the lower panel of **Figure 14**, which shows the resultant probabilistic distribution of predicted LMB mercury concentrations for a load reduction of 17.7 $\mu g/m^2/yr$. (and a current assumed rate of 35 $\mu g/m^2/yr$.).

Note that as more dimensions of parameter uncertainty are included, the likely predicted steady state or long-term response of largemouth bass to the given mercury load reduction becomes increasingly more uncertain.

5.4.5 Atmospheric modeling – Conceptual Issues

The Florida Everglades ecosystem extends over 3,000 square miles and is comprised of many habitat types, thus it was not realistic use the E-MCM to simulate the entire ecosystem. Because the extensive and intensive monitoring studies in the Everglades by USEPA and the US Geological Survey have focused on a mercury “hot spot” in central Water Conservation Area 3, this site was also chosen as the deposition receptor for this analysis. Extensive data were available for 1995-1996; as a result, this period (22 June 1995 to 21 June 1996) was selected as the period of study. Atmospheric deposition rate for 1995-1996 is referred to as “current” deposition rate in this report.

The atmospheric modeling did not attempt to deal with the inferred but ill-characterized long-distance transport of mercury from the global background into Florida. Clearly, long-distance transport from the global background must be presumed to be non-zero, but neither present-day models nor measurements are adequate to estimate the magnitude of this source of mercury to Florida. Only local emissions sources were modeled.

As described in Appendix 1 and in recognition that there are limits to our understanding, tools and data available to support modeling of the global transport of a pollutant, source-receptor modeling relied primarily on local sources to estimate deposition to the Everglades. This has led to no little controversy and comment over the contributing role of local emissions in south Florida to *wet* deposition rates in the Everglades, and has fueled debate as to whether the estimate of the global or 'long distance transport' source to the *total* deposition signal is too uncertain to conclude that local sources are indeed important. The widely divergent estimates of the 'local vs. global' contributions to deposition derived from the FAMS (Guentzel, *et al.*, 2001) and SoFAMMS (Dvonch, *et al.*, 1998) have both illuminated and fueled this debate. It is, however, possible to draw upon the several lines of evidence available to set reasonable bounds around the likely contributions of mercury in Florida.

- Using multivariate receptor modeling, Dvonch, *et al.* (1998) concluded that 71 ± 8% of the wet deposition signal measured at five sites in the Everglades could be accounted for by local sources. Conversely, Guentzel, *et al.* (2001) based on their analysis of seasonal patterns in wet deposition of mercury and the uniform nature of summertime mercury concentrations in rain across the south Florida, as well as source apportionment calculations based on a relatively simple mass balance box model on atmospheric fluxes of reactive gaseous mercury in south Florida, concluded that local sources can account for only 30 to 46% of the wet deposition signal.
- An Everglades-wide sediment coring study begun in 1992 (Rood, *et al.*, 1995) yielded estimates of historical mercury accumulation rates in Everglades soils spanning the period 1900 through *ca.* 1990. Comparison with recent deposition estimates (as $\mu g/m^2/yr$) among comparable Everglades sites from that time to the present are given in the table below:

Rood, *et al.*, 1995	*ca*. 1990	NADP MDN 2002	2001
WCA-1	79	ENR Project	21
WCA-2	59	NA	--
WCA-3	39	Andytown	24
ENP	40	ENP	18

The average mercury accumulation rate in sediment Everglades-wide was 53 $\mu g/m^2/yr$ *ca.*1990 vs. 21 $\mu g/m^2/yr$ from atmospheric deposition in 2001. These data suggest a decline in deposition of ~ 60% overall since *ca*. 1990.

- Everglades largemouth bass (fillet) and great egret (feather) mercury concentrations have declined *ca*. 75% from the mid-1990's to the year 2002.

- Data on potential trends in the 'global background' indicate a "very small downward trend from 1995 through 2000" at Alert, Canada (Schroeder, Pers. Comm., 2002) and there are similar results from Mace Head, Ireland (Ebinghaus, from Schroeder, Pers. Comm., 2002). Both are relatively remote background sites. Published data indicate a decline over the northern Atlantic of ca. 20% by the mid-1990's. (Langer & Slemr, 1991; Slemr, *et al*., 1995; Slemr, 1996; Slemr & Scheel, 1998; Ebinghaus & Slemr, 2000). It is apparent that long-term trends of elemental mercury in the atmosphere at background sites are not of similar magnitude to the declines evident in the Everglades ecosystem.
- An independent analysis by the Florida Electric Power Coordinating Group on trends of mercury emissions and concentrations in south Florida biota (per above) concluded that at this juncture *"…it is clear that the fundamental hypothesis that changes in local emissions of mercury [in southeast Florida] have been the primary agent for recent biota changes in mercury concentrations in the Everglades cannot be rejected."* (Pollman & Porcella, 2002).
- Receptor modeling applied to source and ambient data during the intensive SoFAMMS field study in 1995 indicated that 92 (± 30)% of the total mercury deposition measured at the Davie site near Ft. Lauderdale could be accounted for by local sources (Dvonch, *et al*., 1998).
- The approximate magnitude of the global background contribution can be bounded from the *ca*. 300 rain samples from 17 sites in Dade and Broward counties during the August 1995 SoFAMMS project. Observed minima in background rainfall mercury concentrations at coastal sites in south Florida approximated 5 ng/L. Assuming annual rainfall rates of 130 cm/yr., these concentrations would result in background deposition rates of about 6.5 $\mu g/m^2$/yr., or about 21% of rainfall deposition.
- As reported in herein, comparative model analyses of transport of mercury from all point sources in Florida and adjoining states vs. the 38 point sources in the south Florida modeling domain alone, indicated a contribution to the Everglades from regional sources within the southeastern US of less than 5% of total deposition.
- Contrastingly, the FAMS investigators (Landing, *et al*., 1995, Guentzel, *et al*., 1997, 2001) concluded from the weak trace element signatures in rainfall samples and a box model of mercury fluxes into and over Florida, that local sources alone could not account for the amounts of mercury in measured in rain.

We view the FAMS and SoFAMMS projects as having been complementary, not contradictory. Combined with other information they support the notion that the dominant source term signal contributing to total mercury deposition in south Florida are local emissions.

By our analysis, estimated total deposition for June 1995 – June 1996 was 35.3 $\mu g/m^2$/yr (DEP, 2002), of which 23 $\mu g/m^2$/yr was measured by FAMS as wet deposition and 12.2 $\mu g/m^2$/yr modeled as derived from dry deposition. Dry deposition in south Florida expectedly is greatly dominated by RGM. Since the removal rate of RGM from the lower troposphere is rapid, and because the production rate is low, it is reasonable to assume that the predominant fraction of the dry deposited mercury in the Everglades is local in origin. If we assume that this fraction is 80%, then this equates to a local contribution of 9.8 $\mu g/m^2/yr$. We then take the lowest estimate of 30% from Guentzel, *et al*. (2001) to describe the local emissions contribution to the annual wet deposition of 23.12 $\mu g/m^2/yr$. This equates to a lower limit contribution of 6.9 $\mu g/m^2/yr$ from local emissions.

Combined, the total estimated contribution from local emissions to wet and dry mercury deposition is 16.7 $\mu g/m^2/yr$, or 47% of the total signal. If we ascribe a contribution of 6.5 $\mu g/m^2/yr$ to the global background (as described above), then the maximum that other regional and larger scale sources other than global background can contribute is 34%. If we use the midpoint of the Guentzel, *et al.* (2001) estimate of local contributions to wet deposition (38%), the contributions of each major source category to total deposition are:

- Local sources – 52.5%
- Global background – 18.4%
- Other regional sources – 29.1%

Regardless of whether the FAMS or SoFAMMS analyses discussed above ultimately proves to be closer to the truth, we can use their combined results to constrain a lower limit for the likely contribution of local sources to total deposition. It is our conclusion that the sum of these various lines of argument suggest that at a minimum local sources account for more than 50% of mercury deposited in southern Florida, and several other analyses suggest that the contribution may be substantially greater. Narrowing of these divergent estimates is one of the remaining goals of the SFMSP.

This issue, i.e. not explicitly treating global sources, was the subject of several review comments. The authors maintain, however, that given the present state of understanding of the global mercury cycle, it would be unduly speculative to attempt this. <u>At this time, there are few data at present to constrain a global mercury modeling analysis!</u> For example, it is only within the last two years that the phenomenon of mercury depletion events at polar sunrise has been convincingly established. The magnitude of this sink has been speculated to be important to the global cycle, and the recent nature of its discovery reveals how little we understand atmospheric mercury cycling on the global scale.

To address questions about the potential importance of global background contributions to mercury to south Florida, the UMAQL group evaluated two model scenarios to aid in bounding the potential magnitude. By modeling two regional emissions source scenarios: one included all sources within the Southeastern US (including Florida), the other included only the 38 sources in southern Florida. By difference between the two scenarios, this modeling analysis estimated that sources outside the south Florida region contributed approximately 5% to deposition at the receptor site in near Fort Lauderdale. Because of its estimated small size, sources in the Southeast region outside south Florida were excluded from subsequent analyses.

Three main sources of uncertainty are present in the atmospheric modeling component of this project: source characterization, meteorological variation, and the input parameters specified in the model.

The source emissions inventory is the major source of uncertainty in the atmospheric model. The inventory used was that developed for the USEPA Mercury Study Report to Congress (USEPA, 1997), which was the only comprehensive, self-consistent emissions scenario available. Other emission and speciation scenarios were examined to evaluate their effects on total deposition (see Appendix I). Incorporation of point-source specific data on emission rates and mercury speciation for only two sources in the south Florida region would result in a significantly lower annual deposition rate (Appendix I, **Figure 12**). The apparent discrepancies among emissions data and the emissions scenarios evaluated in all likelihood reflect the rapid decline in mercury emissions occurring during the period of 1985 – 1995. **Figure 15** shows the results of various emissions scenarios on the resulting wet deposition estimates.

Meteorological variation also represents an important source of uncertainty in the model. In the modeling, for each meteorological cluster, two wet days and two dry days were selected for use in the modeling exercise (**Table 8**). Where possible, these days were chosen such that they represented extremes in the spatial nature of the atmospheric transport and deposition for the given cluster. It was believed that in doing so, potential biases from choosing two days with nearly identical deposition patterns would be minimized.

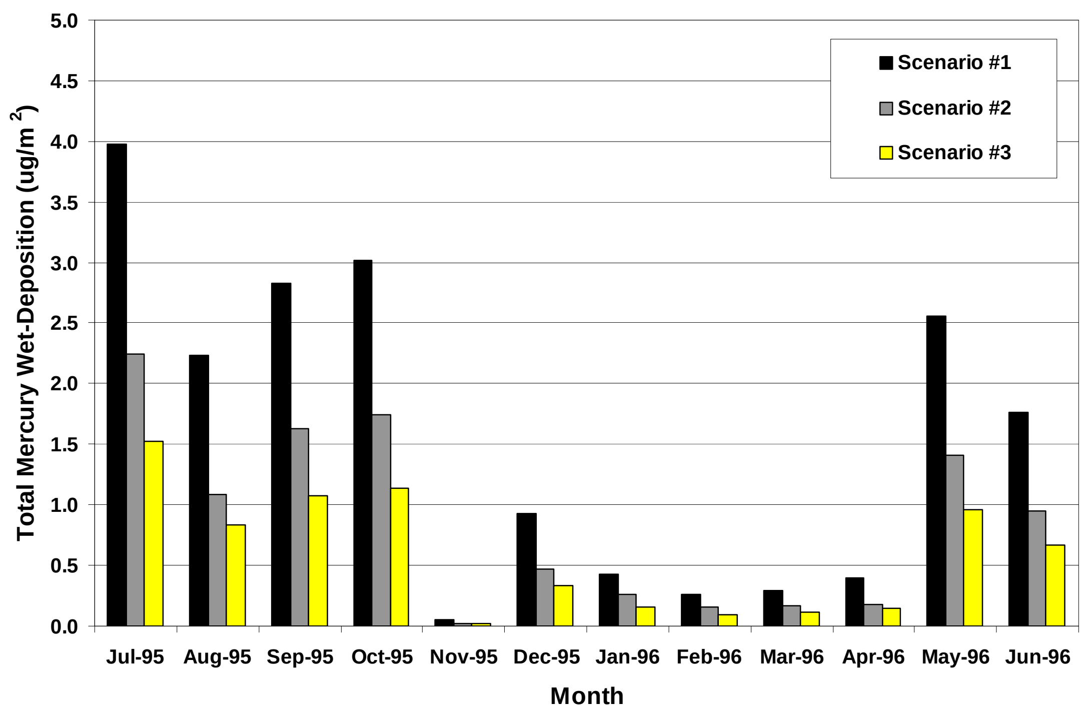

Figure 15. Comparison of the modeled monthly wet deposition to SFWMD WCA 3A-15 as a function of emissions scenario. Scenario #1 corresponds to the emissions inventory derived from the USEPA Mercury Study Report to Congress; Scenarios #2 and #3 reflect adjustment for measured MWC & MWI speciation.

Figure 16 presents the modeled 24-hour total wet deposition estimates for WCA 3A, as a function of atmospheric transport cluster (similar data are discussed in Appendix I for dry deposition). Clusters with predominant offshore flows result in little wet or dry deposition. In contrast, clusters with onshore flows – where the air mass moves over the southeast Florida metropolitan area – produce significant, although variable, deposition. Lack of precision in estimates of wind direction and wind speed could lead to relatively larger errors in estimated deposition to a specific location such as WCA 3A-15. Another factor in the between-cluster variability is the location and magnitude of the emission sources relative to WCA 3A.

Other sources of uncertainty are the values used as inputs for dry deposition rates and the Henry's Law constant. These parameters were used to calibrate the model. Their effects and use in the calibration procedure are discussed in Section 4 of Appendix I.

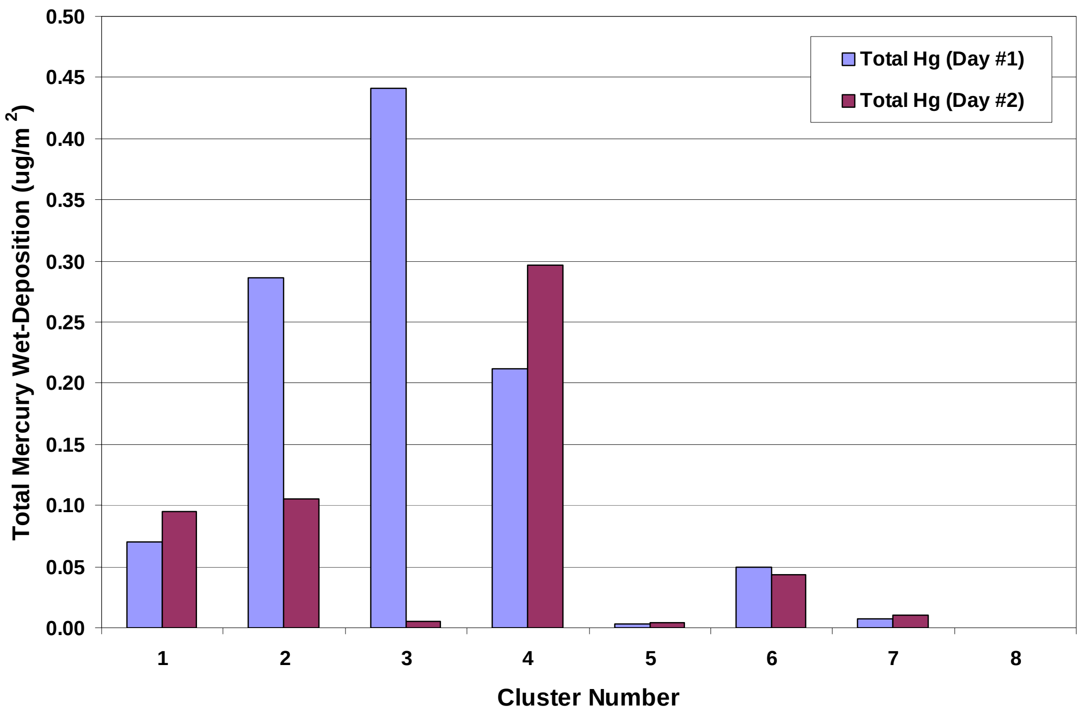

Figure 16. Comparison of the modeled 24-hour wet deposition to SFWMD WCA 3A as a function of atmospheric transport cluster and day within cluster. Days 1 and 2 represent spatial extremes for deposition within a given cluster.

5.4.6 Effects of Uncertainty on Endpoint Predictions

As stated earlier in this section, the treatment of the uncertainties will give us an indication of the power of our present knowledge and, more constructively, guidance for the final phase of SFMSP studies to reduce these uncertainties to acceptable levels. To reiterate, uncertainties in this analysis can be lumped into three broad categories: (1) characterization of emission source rates and speciation, including both local sources and background (hemispheric and global) inputs; (2) the transport, reaction, and deposition of mercury from source to receptor; and (3) the aquatic cycling and fate of mercury once it enters the Everglades.

We evaluated the effects of uncertainty in the estimated wet and dry deposition rates to determine whether errors in the deposition rate used in model calibration to current conditions would fundamentally change the response between assumed changes in atmospheric loading and the endpoint of greatest interest, concentrations of mercury in 3-year old largemouth bass. There is uncertainty inherent in our estimates of average annual wet and dry Hg(II) deposition arising from (but not limited to) analytical and field collection errors, errors induced from extrapolating from sites where mercury wet deposition has been measured to site 3A-15, and errors in modeling source-receptor relationships, including errors in emission estimates and errors in simulating meteorological conditions.

To accommodate uncertainty in the current Hg(II) deposition rates, we calibrated E-MCM separately for three loading scenarios:

- The current mean annual load estimated from the UMAQL hybrid modeling analysis: 31 $\mu g/m^2/yr.$ (modeled wet + modeled dry).
- The upper and lower limits encompassing 95% of the likely estimates for the current modeled total deposition rates: 36.7 and 25.1 $\mu g/m^2/yr.$, respectively.

The UMAQL modeled estimates of total deposition were used for the purposes of this analysis because of the availability of uncertainty in the deposition estimates from the UMAQL analysis. This range of values encompasses the current estimates of total deposition derived from measured wet deposition and modeled dry deposition used in E-MCM simulations, and was thus considered adequate for the purposes of this exercise.

Table 11 summarizes the annual (propagated) uncertainties in wet, dry, and total deposition modeled by UMAQL. These uncertainties were coupled with uncertainties inherent in the estimates of annual wet deposition derived from the FAMS to develop an estimate of the total uncertainty in the wet and dry deposition rates, viz., 9.6% (Appendix II, Section 5.6)

Table 11. Modeled annual wet and dry deposition rates developed by UMAQL and the associated annual uncertainties (standard deviation). Values computed from monthly estimates of each flux component and its inherent uncertainty.

Flux Component	Deposition ($\mu g/m^2/yr.$)	σ ($\mu g/m^2/yr.$)
Modeled Wet Deposition (UMAQL)	18.74	1.57
Modeled Dry Deposition (RGM & particles, UMAQL)	12.20	2.03
Total Deposition	30.94	2.57

For each of the three loading rates, E-MCM was calibrated to achieve the current observed total and methylmercury concentrations in the marsh, including fish. Thus, the predicted fish mercury concentrations were nearly identical in each calibration, but some rate constants by necessity were altered between scenarios to yield reasonable calibrations. Once the model was calibrated for each of the loading scenarios, we tested whether different calibrations yielded substantially different response curves. The comparisons were based on examining whether the same fractional reductions in deposition yielded the same long-term response. As shown in **Figure 17**, the uncertainty regarding the true loading rate has little effect on the timing or magnitude of the response of age 3 largemouth bass to load reductions of 50%. Results were similar for load reductions of 15% and 75%.

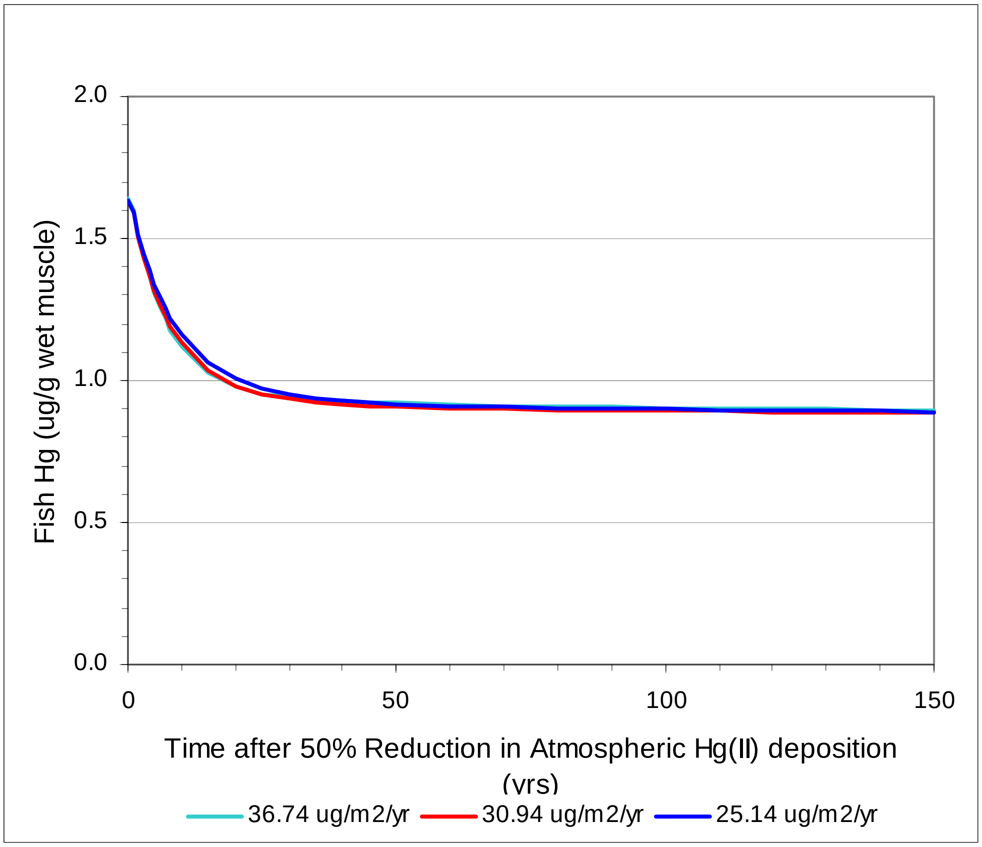

Figure 17. E-MCM predictions on the dynamic response of age 3 largemouth bass mercury concentrations to a 50% reduction in atmospheric Hg(II) deposition. Results are shown for three calibrations: lower 95% estimate, best estimate from UMAQL hybrid modeling analysis, and upper 95%.

The effects of uncertainty in our current modeled estimates of atmospheric deposition of mercury thus appear to have little or no effect when we examine how changing the *total* atmospheric load by a fractional amount[10] will influence the dynamics and magnitude of biotic response. It is important to realize that this conclusion is only valid within the framework of the underlying assumptions used to conduct the analysis. Perhaps most important is the assumption that upstream loads are changed fractionally in the same way and at the same rate as the atmospheric load. Clearly, the temporal response of the watershed is slower than the atmospheric pool to changes in emissions and loading. As of this writing, there are currently few data from dose-response experimental studies on catchments and wetlands (including the Everglades) in North America. Studies to elucidate the likely temporal response to changes in loading will be a major focus of the *Mercury Experiment To Assess Atmospheric Loading in Canada and the United States* (METAALICUS) in the

[10] To reiterate, the focal point of this conclusion is that depending upon the assumed atmospheric deposition rate used to calibrate the model, E-MCM will yield different responses in fish tissue mercury to identical (i.e., mass) magnitudes of reductions of mercury loading. Thus reducing regional emissions by 10 $\mu g/m^2/yr$ for the low deposition estimate scenario would result in a larger percentage reduction in fish tissue mercury than that predicted for the high deposition estimate scenario.

Experimental Lakes Area in northwestern Ontario, and the stable isotope mesocosm studies conducted *in situ* by ACME in the Everglades. Both studies are currently underway. Preliminary data for the Everglades indicate that an increase in Hg(II) loading produces a linear increase in MeHg in surface sediments and in fish. However, the slope of the response was highly variable among sites. Finally, this analysis does not resolve the question of how our uncertainty about the nature of all the sources contributing to mercury deposition in the Everglades affects the local source-receptor relationships developed in this analysis.

This analysis also illustrates another issue reflecting the state-of-the-art of calibration of E-MCM: *viz.,* given that nearly identical simulation results can be obtained for three significantly different source loading rate scenarios (the upper loading rate estimate differed from the lower estimate by a nearly a factor of 50%), the model is not as well-constrained or robust as desired. The greatest difficulty when calibrating the Hg(II) component of the model lies in our uncertainty of sedimentary mercury accumulation rates. Once the Hg(II) component of the model is calibrated, the methylmercury cycle is not as well constrained as desired. For example, the rates of methylation and demethylation are still inadequately quantified, and different combinations of these two fluxes could still be combined to ultimately result in the same concentrations in fish. The major removal mechanism for total mercury from the study site was burial in the deep sediments, and our uncertainty in these rates based on available measurements is easily greater than 50%. Other variables in the model help constrain the calibration, but there is still too much uncertainty in this key loss pathway to ensure a more robust calibration.

5.4.7 Effects of Annual Variability in Atmospheric Deposition Rates on Endpoint Predictions

Even if the relationship between emissions and deposition was known exactly, and emissions remained unilaterally constant with time, year-to-year variability in mercury deposition will occur due to changing meteorological and precipitation patterns. This in turn expectedly would produce year-to-year variations in largemouth bass mercury concentrations. To address the effects of this variability, an artificial data set of atmospheric deposition of mercury was synthesized based on annual variability observed at three Everglades sites during FAMS (Appendix II, Section 4.5 describes the approach and Section 6.5 describes the results). These sites had comprehensive deposition data spanning 2 - 4 year periods. The synthesized data set, which comprised 500 annual values for total mercury deposition, had log normal distribution characteristics with the desired mean and standard deviation values derived from the FAMS sites.

Inherent in this approach were several key assumptions:

- Deposition is constant over the long-term but varies annually about some mean value, and can be described statistically as a lognormal distribution.
- Wet deposition rates measured at the Florida Atmospheric Mercury Study (FAMS) south Florida sites between 1993 and 1996 are adequate to describe the variance of this distribution.
- The coefficient of variation for total deposition is similar to values measured for wet deposition rates.

- Inflowing (upstream) MeHg and Hg_{tot} loads vary in proportion to wet Hg_{tot} deposition.

An average coefficient of variation of 26.4% was calculated for the three FAMS sites. The synthetic total deposition data set was then constructed based on the estimated annual average total mercury deposition rate of 35 $\mu g/m^2$/yr. (FAMS wet + modeled dry) developed in Appendix I. Variations in largemouth bass mercury concentrations were then computed by first running E-MCM with a fixed deposition rate of 35 $\mu g/m^2$/yr. for 200 years to achieve steady state conditions. Using the synthesized total deposition data set to simulate annual deposition variability, the model was then run an additional 500 years, with fish mercury concentrations recorded each year.

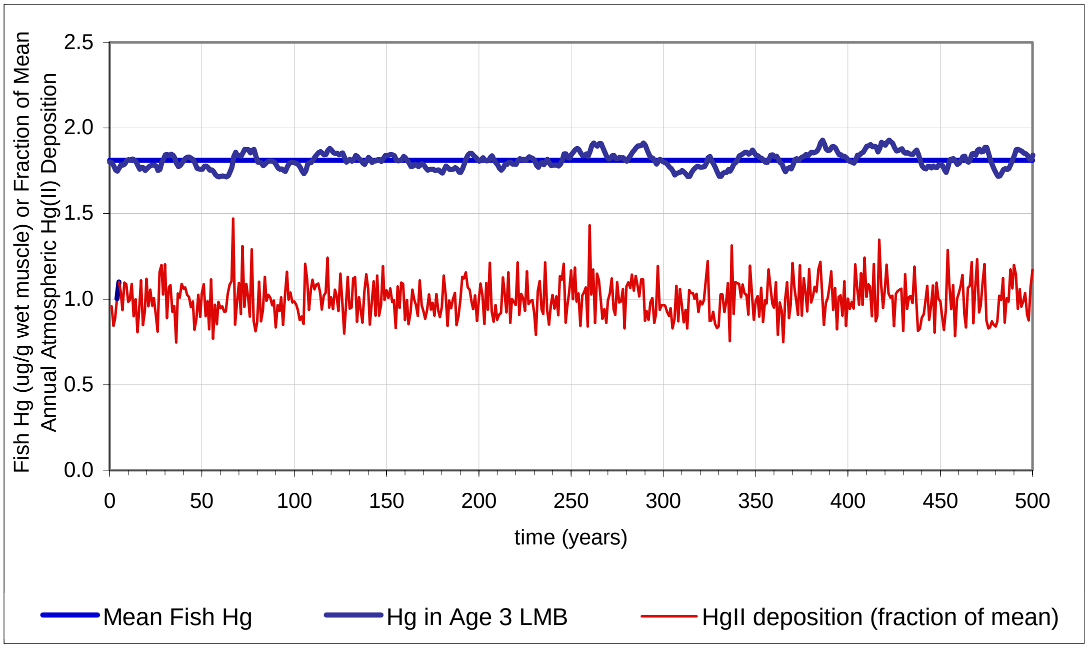

Figure 18. Input annual atmospheric Hg(II) deposition rates and predicted Hg concentrations in age 3 largemouth bass for 500 year simulation.

Figure 18 gives the results from a long-term simulation. Under current deposition, the model calibrated concentration for mercury in 3-year old large mouth bass is 1.81 mg/kg, with a coefficient of variation of 3.6%. Compared to the variance in the deposition rates, the response of the bass was considerably damped, and reflects: (1) buffering against short-term changes by the sediment pool of mercury, which greatly exceeds the amount of mercury entering the system on an areal basis any given year; and (2) the fact that fish tissue concentrations reflect an integrated response over the 3 years of varying exposure, rather than simply reflecting the current year deposition rate.

6 CONCLUSIONS, RESEARCH NEEDS AND PLANS

The primary objective of this pilot study was to explore how a TMDL or critical loading analysis could be conducted when the pollutant of interest enters aquatic ecosystems largely through atmospheric deposition. In brief, a hybridized approach concatenating an atmospheric model with an aquatic mercury cycling model was used to predict the relationship between local emissions, deposition and, ultimately, mercury concentrations in largemouth bass at an Everglades site known to have elevated mercury concentrations in fish tissue.

This study synthesizes and integrates data from arguably one of the most comprehensive field measurement and monitoring programs conducted on the fate and transport of an environmental pollutant. Nonetheless, we recognize that numerous areas of uncertainty remain in the models' formulations and the data they rely on, and both the model and data uncertainties identified in this report are guiding future research of the South Florida Mercury Science Program.

This combined modeling analysis successfully integrated a multimedia modeling approach with extensive field data to produce simulations that reasonably agree with conditions and changes seen in the south Florida region. For example, since the mid-1980's emissions of mercury have declined dramatically. Similarly, monitoring data from the mid-1990's to the present show significant declines in mercury in Everglades fish and wading birds. The timing of trends and rapidity of response seen in the biota appear consistent with: (1) the role of local sources as an important driver of atmospheric deposition as indicated by the UMAQL modeling; (2) the apparent decline in local emissions in south Florida inferred from limited municipal solid waste incinerator emissions data compiled by DEP; and (3) E-MCM modeling of the timing of change.

Overall, E-MCM was calibrated to fit observations for total and methylmercury at WCA 3A-15. Regarding the model simulations:

1. The E-MCM model predicts a linear relationship between atmospheric mercury deposition and mercury concentrations in largemouth bass, with a small residual mercury

concentration in fish at zero atmospheric mercury deposition (Figure 9). In other words, for any reduction in mercury inputs there may be a near 1:1 reduction in fish mercury concentrations. Furthermore, error analysis shows that the E-MCM predicts equivalence between the percent decrease in atmospheric mercury deposition rate and the percent decrease in largemouth bass mercury concentration over the likely range for current estimates of atmospheric deposition of mercury. The slight offset from a 1:1 relationship is a result of movement of historically deposited mercury from deeper sediment layers to the water column. Until this mercury is buried below the active zone, it can continue to cycle through the system. In addition, because mercury is a naturally occurring element, fish tissue mercury concentrations can never be reduced to zero.

2. In the absence of changes to the system other than mercury loading (e.g. changes in sulfur cycling, nutrient cycling, or hydrology), a reduction of about 80% of current total (1995-96) annual mercury atmospheric deposition rates would be needed for the mercury concentrations in a 3-year old largemouth bass at WCA 3A-15 to be reduced to less than Florida's present fish consumption advisory action level of 0.5 mg/kg (parts per million). This modeling did not attempt to deal with long distance transport of mercury from the global background into Florida. Clearly, long-distance transport from the global background must be presumed to be non-zero, but neither present-day models nor measurements are sufficient to estimate the magnitude of this source of mercury to Florida. From the 1995 SoFAMMS project, we can estimate that background mercury concentrations in rainfall at coastal sites in south Florida approximate 5 ng/L. Assuming annual rainfall rates of 130 cm/yr., these concentrations would result in background deposition rates equal to 6.5 $\mu g/m^2/yr$. If, as predicted by the UMAQL hybrid model/FAMS analysis, current loading rates are indeed *ca.* 35 $\mu g/m^2/yr$., this rate of background deposition (i.e., 21% of total loading) suggests that to reach a target of age-3 largemouth bass average concentrations not exceeding 0.5 mg/kg wet muscle for an average year would require virtually complete elimination of local atmospheric deposition sources of mercury.

3. Mercury concentrations in age-3 largemouth bass are predicted to achieve 50% of their long-term, steady state response within approximately 10 years and 90% within *ca.* 30 years following sustained mercury load reductions. The time it should take to reach 50% or 90% of final steady-state fish mercury concentrations following a reduction in mercury deposition is independent of the actual magnitude of the decrease. In other words, it takes about 10 years and *ca.* 30 years to reach about 50% and 90% of the ultimate steady-state fish mercury concentration, respectively, whether the reduction is 85% or 25% of the current mercury deposition rates. The time scale of this response is quite sensitive to the turnover rate of mercury in the surficial sediments. Factors which increase the flux of detrital material to the sediments (e.g., eutrophication) will result in a faster response time as elevated mercury in the sediment pool is buried deeper and more rapidly.

Further Work in Progress or Planned

There are a number of research efforts underway or planned to improve the capability of the combined atmospheric modeling and aquatic modeling approach.

The mercury contribution from background (hemispheric or global) sources is unknown, and directly affects both the estimates of atmospheric deposition to the study site, and the response of the system to given changes in the magnitude of the current load. The present analysis excludes consideration of long-distance transport of mercury into Florida because the present state of global models and measurements do not give us any basis for doing so. When this modeling study was performed, there were no measurement data of mercury species at several altitudes to incorporate long-distance transport in a quantitative manner. Until measurements or models allow us to constrain the uncertainties in the long-distance transport phenomenon, there is no objective basis for addressing this question.

Note: USEPA, DEP and NOAA-ARL conducted winter and summer aircraft campaigns to measure the relevant mercury species in and above the marine boundary layer off the east coast of Florida which should allow parameterization of this source term. Results of this investigation should be completed in 2002.

Previous research has suggested that the atmospheric deposition of mercury to south Florida is dominated by wet deposition, with the majority of this deposition associated with summertime convective precipitation events (Guentzel *et al.*, 1995, 2001; Dvonch *et al.*, 1999). The modeled analysis of dry deposition conducted as part of this study, however, suggests that dry deposition is important as well, comprising perhaps 34 to 40% of the total mercury deposition signal. Currently, only very limited data are available to assess this component more directly.

Note: The Florida Everglades Dry Deposition Study (FEDDS) conducted winter and summer field campaigns in 1999 and 2000, respectively, and, when data analysis and modeling is completed, these results should improve both knowledge of depositional processes and parameterization of models.

If all current atmospheric loadings of Hg(II) to the marsh surface were eliminated, regardless of source, our analysis suggests that fish mercury concentrations would still be *ca.* 6 % of current values, at least over the next 100 years. Only a fraction of this is due to continued deposition of MeHg, which, based on limited measurements, appears to comprise less than 1% of the estimated current total atmospheric mercury load. Most of the continued supply of mercury appears to be internal through remobilization of Hg(II) and methylmercury from deep sediment layers via porewater uptake by macrophytes. Over the course of 100 years, Hg(II) and methylmercury concentrations in these deeper sediments are not significantly affected by changes in atmospheric mercury deposition in the simulations. This in essence adds another source of mercury to the overlying active marsh system, a source which would slowly diminish in the absence of atmospheric

Hg(II) deposition. This assumption should be critically reviewed in any future assessments.

Note: DEP and USEPA have initiated further analyses of potential sources of MeHg in rain and of MeHg in rainfall at multiple sites in the Everglades to confirm initial estimates of rainfall MeHg from FAMS. This will allow better parameterization of this term in future assessments. The stable isotope mesocosm studies currently conducted by USGS ACME team (Krabbenhoft & Gilmour, 2002) should further identify the nature of the dose-response relationship and the role of internal remobilization of legacy mercury on recovery.

A second major objective of this study is to identify major sources of uncertainty in our model predictions that would adversely influence our ability to reliably assess the relationship between local mercury emission sources and biotic response. Excluding errors relating to source characterization, modeled annual total mercury deposition rates had an estimated error of 8.3%. As illustrated earlier, the large uncertainties in source emission characterization (quantity and speciation) have a very pronounced effect on modeled deposition rates.

Note: It is clear that one of the most critical areas for future investigation is resolving the divergences in present mercury emissions inventories. Further work in this area is underway

A number of aquatic cycling process and other factors presently are not well understood and are not fully developed in the E-MCM. For example, the sulfur cycle, e.g. sulfide-mercury interactions, in the Everglades is anthropogenically perturbed and poorly understood. Proper representation of sulfur chemistry in sediments could change the shape and the slope of the atmospheric loading-biotic response curve). The response curve slope produced in this analysis differs from unity regarding relative response to relative changes in loading largely because the model predicts that "legacy" mercury stored deep in the sediments (5 to 20 cm below the sediment-water interface) is mobilized and brought into the water column by macrophyte roots. Based on current sedimentation rates, this material will not be removed from the system for perhaps hundreds of years.

Note: An improved representation of sulfur cycling and chemistry is presently being developed for the E-MCM and will be available for subsequent analyses.

The E-MCM model also has inherent uncertainties that affect the predicted response of largemouth bass to changes in mercury loadings. Sensitivity analysis identified a number of key parameters to which the model is quite sensitive, including particulate fluxes relating to vegetation cover and suspended solids, sediment methylation and demethylation rates, and factors affecting fish diets and growth. Based on current limits of uncertainty in parameter values, the E-MCM is most sensitive to the uncertainty in parameters that relate to methylation and demethylation. However, to fully assess the effect of parameter uncertainty in E-MCM, including inputs for mercury loading from atmospheric deposition, a Monte Carlo analysis ideally would be conducted in which each model parameter is varied according to its likely distribution. Such capabilities in E-MCM were not available for this study. Nonetheless, the joint or combined effect of uncertainty in just two parameters (Figure 14) can be illustrated for predicted responses of largemouth bass to changes in atmospheric loading.

Note: Monte Carlo analysis routines are being developed for the E-MCM and will be available for subsequent analyses.

Based on the analyses presented herein it is evident that there is great potential for combining such air and water modeling approaches for TMDLs involving air deposition of mercury for other aquatic ecosystems. Although mercury was used as the 'model' pollutant for exploring how this type of TMDL analysis could be conducted, many of the limitations and successes that emerged in the application of the method for mercury likely are applicable to analyses that may be conducted for other impaired waters where the pollutants of concern are significantly of atmospheric origin (e.g. NOx, PCBs).

The progress represented in these demonstrations of a unique combination of atmospheric and aquatic cycling models is gratifying. Because this document represents the drawing together of many elements of monitoring and research programs, the preceding discussion has identified and dwelt on a number of areas where uncertainty remains. There is reason to believe that, with modest additional effort, these remaining uncertainties can be reduced to levels that will allow reasonable allocation of mercury emissions so as to protect the designated uses of affected waters.

6.1.1 Conclusions

This study has demonstrated the utility of using linked atmospheric and aquatic mercury cycling models to evaluate critical loading rates for an atmospherically derived pollutant (i.e., mercury). Important, if preliminary, information from this modeling indicates that the aquatic cycling of mercury is strongly influenced by changes in the atmospheric load, and that the ecosystem responds in a direct and rapid fashion to changes in load. This study also constructively reveals where uncertainties remain in the state-of-the-art for both the atmospheric and aquatic cycling models, and show what additional information is needed to improve subsequent analysis:

1. Based on the E-MCM model, the fundamental response of largemouth bass to long-term changes in atmospheric deposition of mercury appears insensitive to estimation errors of current levels of wet and dry deposition used during model calibration. This lack of sensitivity largely reflects our uncertainty in actual sedimentary mercury burial rates, coupled with the fact that this pathway is the major removal mechanism for mercury in the system. The predicted response is essentially linear, with calibrations to different assumed current atmospheric deposition rates yielding equivalent responses to imposed fractional reductions in deposition.
2. Sensitivity analyses indicate that E-MCM predictions are most sensitive to uncertainties associated with methylation and demethylation rates, particle and vegetation fluxes, loading rates of Hg(II), and factors affecting fish diet and growth.

Although the exercise of using differing calibrations based on uncertainties in current atmospheric deposition rates produced essentially equivalent mercury loading-largemouth bass response curves, we cannot extend that conclusion further. For example, changes in the assumed particle and vegetation fluxes may render model calibration problematic, and may suggest that other pathways for removing mercury from the system must be operating. The final calibration for E-MCM indicates that the primary removal mechanism for mercury at site 3A-15 is burial, and that sediment turnover rates govern the response time. Changing model calibrations that result in changes in sediment dynamics likely will have a profound effect on the predicted rate of response of the system to changes in atmospheric loading. Thus, further research on these model-sensitive parameters is required to more adequately define the relationship between loading and biotic response.

3. Year-to-year variations in atmospheric deposition to the Everglades are expected to be large (coefficient of variation = 26.3%), even if local emission rates remain essentially constant, due to year-to-year variations in meteorological and precipitation patterns. The impact of these variations on age 3 (and higher ages) largemouth bass mercury concentrations likely will be considerably dampened, both because of sediment buffering and because the concentrations of mercury in older fish reflect long-term integration of varying exposure levels. The lack of a long term Hg(II) deposition data set required us to synthesize a data set to estimate the effects of year-to year variations in Hg(II) deposition. Longer periods of record will be helpful for any future assessments.

4. The E-MCM model was calibrated by assuming current conditions reflect a quasi-steady state. There is accumulating evidence from studies both on mercury concentrations in largemouth bass and wading birds in the Everglades that this is not true – that the system appears to be undergoing a declining trend in mercury concentrations in fish and birds. Under ideal circumstances, E-MCM would have been calibrated to a long-term data set. Unfortunately, such long-term water chemistry and biota data sets do not exist, nor do high-quality, high-resolution mercury deposition and sediment accumulation rate data. This currently precludes a long-term, historical calibration, and was the impetus for choosing a quasi steady-state calibration.

5. Local emission rates and speciation used to predict atmospheric loading rates to the Everglades have a profound effect on the predicted results. The hybrid model simulations (which used south Florida point source emissions derived from the USEPA Mercury Study Report to Congress emissions database) resulted in a modeled total deposition rate of 31 $\mu g/m^2/yr$. Simply changing the emission rate of the two significant sources in Dade county to reflect actual stack testing speciation and rate data measured by Dvonch, *et al.* (1999) resulted in a 43% lowering of the modeled total deposition rate. These results would suggest that any attribution of hemispheric and global sources is very sensitive to parameterization of emissions speciation and atmospheric conversion. This uncertainty has obvious implications regarding the efficacy of controlling local sources to mitigate the current mercury problem in the Everglades. Thus, additional efforts to both assess source magnitudes and speciation,

and to characterize background rates of deposition, are critical if the TMDL process is to be successful.

7 RECENT TRENDS IN MERCURY EMISSIONS, DEPOSITION AND CONCENTRATIONS IN BIOTA

Over the past decade, progressive, statistically significant declines in mercury concentrations have been observed in both largemouth bass and great egret nestlings in a number of sites located throughout the Everglades (Pollman et al., 2002; Frederick et al., 2001). Coincident with these declines have been marked declines in local emissions of mercury (RMB Consulting & Research, 2002; Husar and Husar, 2002). Given that atmospheric deposition is the major source of Hg to the Everglades (Stober et al., 2001), and because local emissions have been postulated as the predominant source of mercury deposited in south Florida rainfall, including the Everglades (Dvonch et al., 1999), the question arises whether the observed declines in biota Hg concentrations can be related to declines in local emissions. This chapter reviews the existing data on mercury emissions, deposition, and biota trends in south Florida in order to address this question. Much of this discussion is based on work previously published by Pollman et al. (2002) and Pollman and Porcella (2003), but extends that work by including more recently available, longer time series for biota concentrations, as well as incorporating new analyses on wet deposition trends for mercury and some exploratory model hindcasting to examine the relationship between emissions and deposition, and aquatic biota response.

Trends in Mercury Emissions

Two fundamentally different types of analyses have been conducted to reconstruct recent trends of mercury emissions in south Florida. The first was a direct approach where a historical emissions inventory was compiled for the period 1980 to 2000 for Broward, Dade and Palm Beach Counties (RMB Consulting & Research, 2002). Emissions were estimated from plant operational data and emission factors typical for the source under consideration. These counties were selected as the region containing sources most likely to be important local contributors to mercury deposition in the Everglades and south Florida. The second approach was an inferential or indirect approach, where the trend in local emissions was inferred by reconstructing a mass balance on the flows of Hg ascribed to various use categories or major economic sectors (Husar and Husar, 2002). This latter analysis first focused on Hg use on a national scale, beginning in 1850 and continuing to 2000, then reduced the scale of analysis to the state level for Florida, and finally concluded with a regional analysis for the Broward, Dade, and Palm Beach counties for the period 1950 through 2000.

The emissions estimates compiled by RMB Consulting & Research (2002) indicated very large changes occurred between 1980-2000 as a function of the major combustion sources in south Florida (power generation, sugar industry, incineration of municipal and medical wastes; Figure 19). Total emissions were quite low between 1980-1982, and then increased in 1983 by 3.5 times above 1982 levels as both municipal waste combustors (MWC's) and medical waste incinerators (MWI's) came on line. Local emissions continued to increase through the 1980's until 1991, when a peak emission flux of nearly 3,100 kg/yr of total Hg was estimated. Throughout the peak emission period of 1983-1991, local Hg emissions originated primarily from MWI's (54 to 76% of the total), and MWI 's and MWC's combined comprised 92 to 96% of the total. Power generation was never above 0.4%, while sugar processing accounted for 4 to 8% of the estimated emissions.

As more stringent regulatory requirements took effect in mid-1992, many MWI's ceased operations, and medical waste was either sent offsite for processing, autoclaved, or landfilled. As a result, local emissions declined sharply through 1993 (65% compared to 1991 levels), followed by a slower and nearly monotonic rate of decline through 2000. The total estimated decline in local emissions between 1991 and 2000 is 2,846 kg/yr, which equates to a total reduction of 93%.

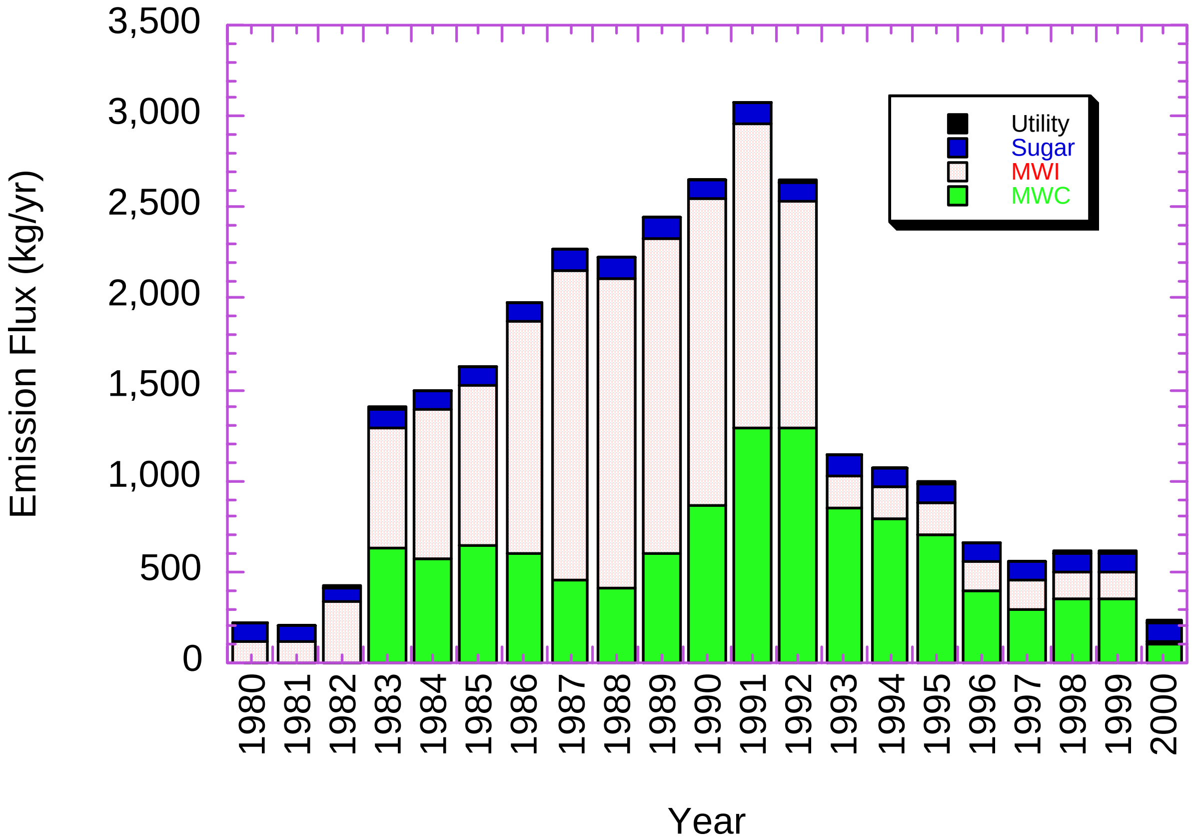

Figure 19. Annual mercury emissions in south Florida, 1980 – 2000, estimated by RMB Associates & Consulting (2002) as a function of major combustion source category. Sources include power generation facilities (Utility), municipal waste combustors (MWC), medical waste incinerators (MWI), and sugar refineries (Sugar).

Figure 20 shows the results from the materials flows analysis conducted by Husar and Husar (2002) for Broward, Dade, and Palm Beach counties. Use categories that contributed most greatly to the flow of mercury through south Florida included electrical (e.g., batteries, lighting, and switches), laboratory use, and control (measuring and control instruments) categories. Although coal is the largest source (45%; 65 Mg/yr) of Hg emissions for the US (144 Mg/yr), no coal combustion occurs in south Florida and only oil and product-related emissions occur.

The total mercury mobilization from electrical, laboratory use, and control categories is depicted in Figure 20 as a solid line ranging from a high of about 18,000 kg/yr in the 1980s and decreasing to <2,000 kg/yr in 1997. A somewhat uncertain fraction of this mobilized mercury is emitted to the atmosphere and, as a result, inferred emission fluxes based on assumed incineration rates of 15 and 30% of the total usage flux are included in the analysis. Also shown in Figure 20 are the direct emission estimates for MSW's and the combined flux from MWC's and MWI's from the RMB analysis. Both analyses show large declines in local emissions approximating 90% relative to peak emissions and the conclusion that local emissions have declined significantly appears reasonably robust. Estimated emissions from both studies agree well after 1993, but differ with respect to the timing of peak emissions.

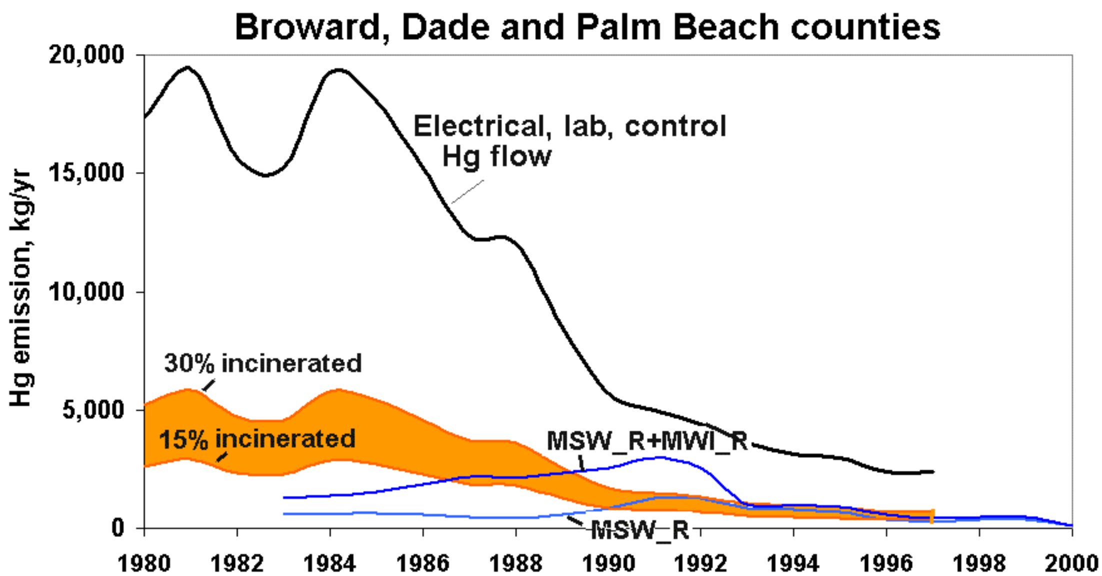

Figure 20. Waste incineration emissions for Dade, Broward, and Palm Beach counties inferred from analysis of mercury usage, 1980 to 1997. Upper line shows annual total mercury usage based on different usages. Emission fluxes are based on 30% and 15% incineration rates (complete mobilization of combusted fraction). Plot also shows emissions for MSW and combined MSW and MWI sources estimated by RMB Associates & Consulting (2002). From Pollman et al. (2002).

Trends in Atmospheric Deposition of Mercury

An essentially continuous record of wet deposition fluxes and concentrations are available from November 1993 through December 2002 at the Beard Research Center in Everglades National Park as part of the Florida Atmospheric Hg Study (FAMS, 1993-1996) and as part of the Mercury Deposition Network (MDN, 1996-2002; http://nadp.sws.uiuc.edu/mdn). The FAMS data consist of integrated monthly wet deposition measurements (Guentzel et al., 2002), while the MDN data consist of integrated weekly samples. During 1996, monitoring from both studies overlapped for the entire year, and comparison of monthly results demonstrated excellent agreement between the two programs (Pollman and Porcella, 2002). As a result, we combined the two studies to form a period of record of eight full years.

Smoothed time series were constructed for Hg deposition, rainfall depth, and volume weighted mean (VWM) Hg concentrations in wet deposition using 12-month running averages derived from the integrated FAMS-MDN data set (Figure 21 and Figure 22). As illustrated in Figure 21, rainfall depth and deposition flux are very closely related[11], and it is difficult to discern without further analysis whether any declines in wet deposition fluxes have occurred unrelated to changes in precipitation. Changes in VWM Hg concentrations are a less ambiguous indicator of whether changes in the atmospheric mercury signal have occurred, although precipitation depth does exert some influence on wet deposition concentrations through washout, particularly when the sample integration period is short. Plotting the running average annual VWM as a function of time indicates that VWM Hg concentrations have declined by 25% since late 1993.

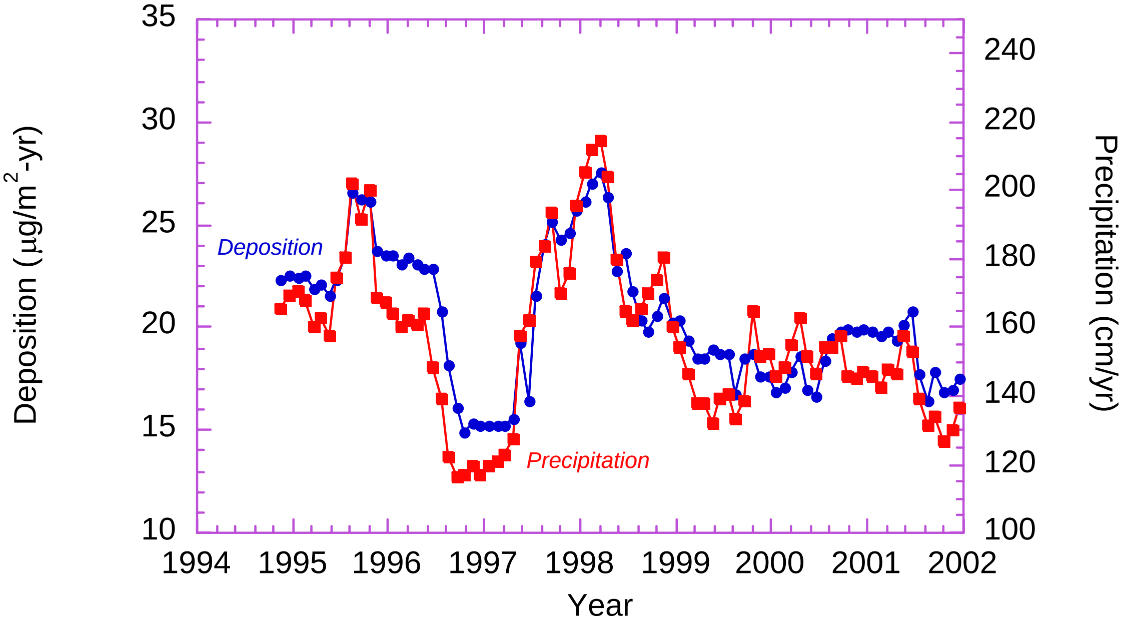

Figure 21. Annual precipitation depth and wet deposition fluxes of mercury measured at Beard Research Station in Everglades National Park, 1993 – 2002. Data are plotted on a monthly basis as the 12-month running total flux or depth. Data are from the FAMS study (Guentzel et al., 2002) and the MDN network.

An alternative analytical approach using analysis of variance (ANOVA; SAS, 1995) was used to eliminate possible confounding effects of both rainfall depth and seasonal dynamics on wet deposition concentrations. Guentzel et al. (2002) demonstrated that very strong seasonal dynamics consistently underlie wet deposition mercury concentrations in Florida within any given year; as a result, a seasonal dummy variable based on a sinusoidal transformation on the month of year the sample was collected was created and input to the model. The dummy variable had the following form:

[11] This is, of course, because deposition fluxes are the product of the weekly volume-weighted mean concentration and the rainfall depth.

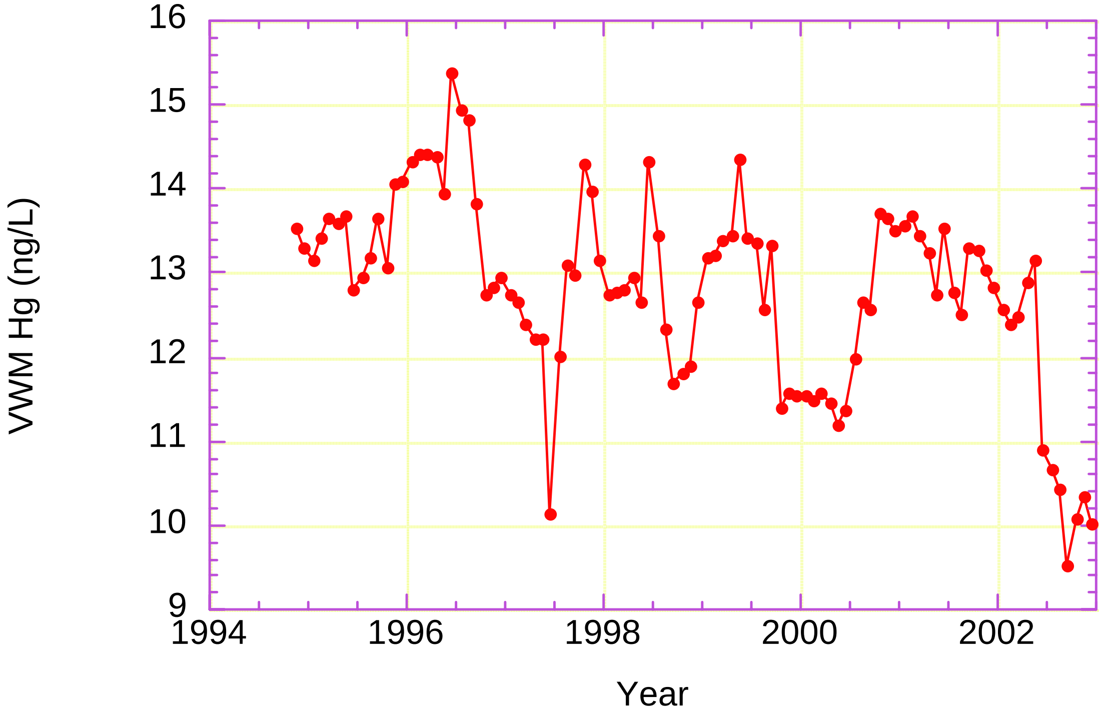

Figure 22. Annual volume weighted mean (VWM) Hg concentration in wet deposition at Beard Research Station in Everglades National Park. Plotted on a monthly basis is the 12-month running average VWM concentration. Data are from the FAMS study (Guentzel et al., 2002) and the MDN network.

$$D_{month} = A \cdot \sin(\frac{M^{*} \cdot \pi}{12}) + B$$

where *A* and *B* are fitted using non linear least squares regression (SAS, 1995) and are equal to 8.8827 and 6.6954, respectively, and M^* is the number of the month (*viz*., 1 through 12), adjusted using a one month offset so that predicted and observed peak values occurred during the same month. Residuals from the ANOVA model for VWM Hg plotted as a function of time are shown in Figure 23 and demonstrate that a statistically significant decline (p = 0. 0413) in VWM Hg concentrations occurred over the period of record. Between 1994 and 2002, the analysis indicates that VWM Hg concentrations declined by approximately 3 ng/L due to factors other than seasonal dynamics and precipitation.

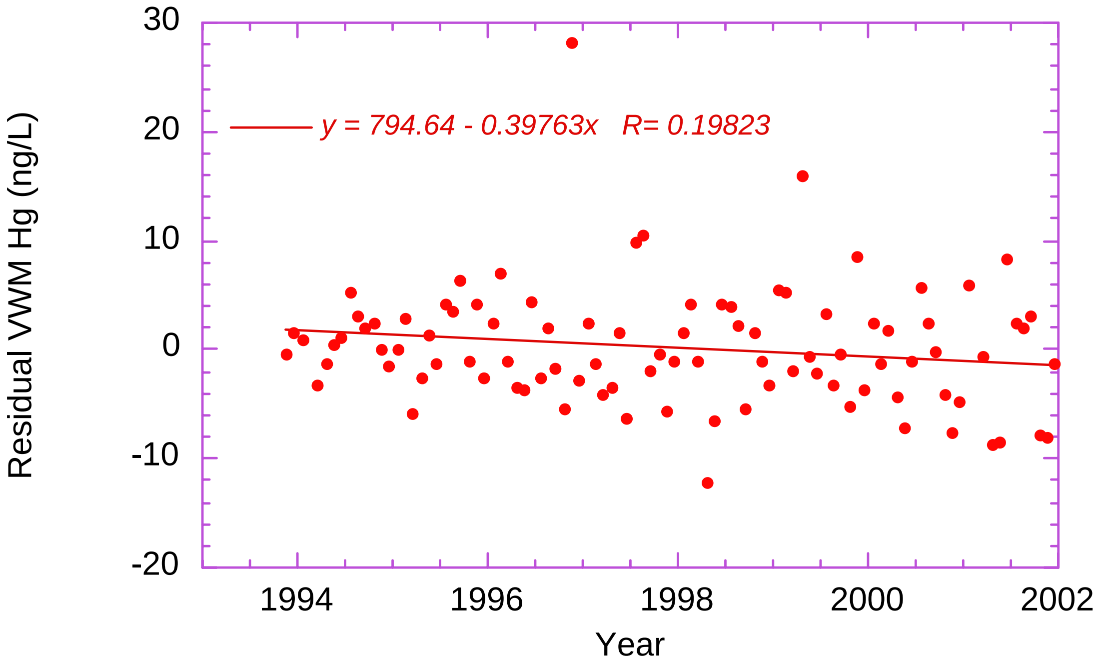

Figure 23. Plot of monthly residuals of ANOVA model of Hg deposition as a function of time. Slope of regression line is significant at *p* = 0.0413.

The declines in measured VWM concentrations are considerably smaller than the overall decline in local emissions estimated to have occurred since the late 1980's and early 1990's (Figure 19 and Figure 20). However, most of the decline in emissions occurred prior to late 1993 when monitoring of mercury concentrations in wet deposition first began. Indeed, the relatively modest change in VWM concentrations agrees reasonably well with the emissions declines after 1993 (Figure 24).

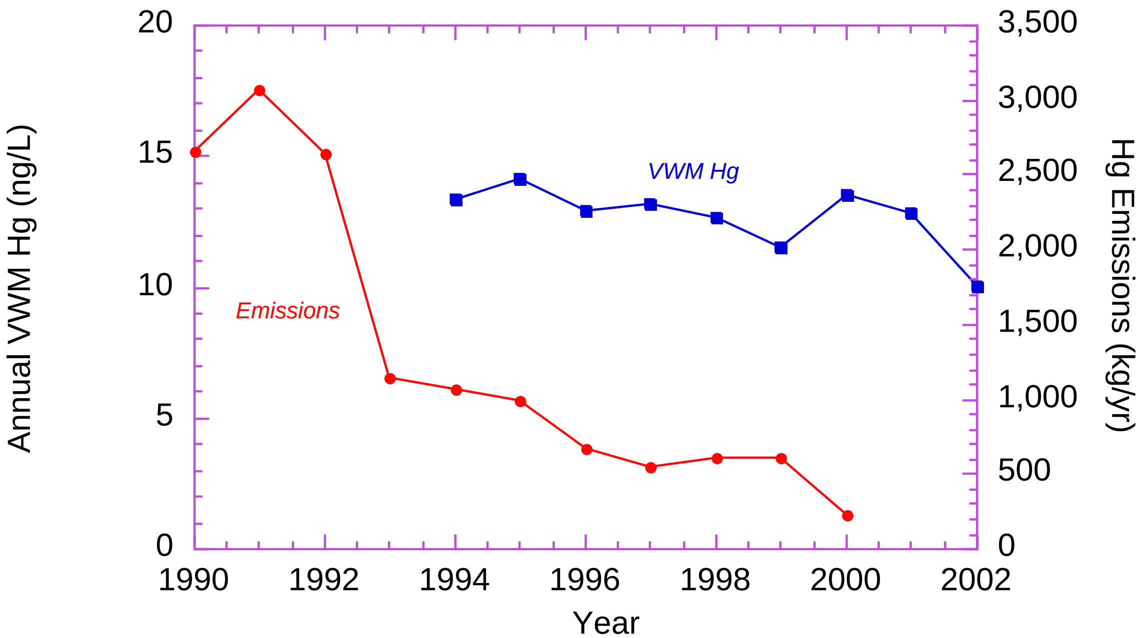

Figure 24. Annual VWM concentrations of mercury measured in wet deposition at Beard Research Center, Everglades National Park, and estimated mercury emissions from Dade, Broward, and Palm Beach counties. Emissions estimates from RMB Consulting & Research (2002).

Trends in Mercury Concentrations in Biota

Two different data sets are available to examine recent trends in mercury concentrations in biota in the Everglades: (1) the unpublished data of Lange et al. (T. Lange, pers. comm.), who have collected and analyzed largemouth bass for tissue concentrations of Hg from sites throughout Florida; and (2) the data of Frederick et al. (2001), who examined Hg concentrations in the feathers of great egret chicks, also throughout Florida and including seven sites in south Florida. Pollman et al. (2002) analyzed the significance of biota temporal trends using the Mann-Kendall Slope Test-of-Sign. This method is a non-parametric test for zero slope that calculates the slope for each possible pairwise combination of observations in the data set, and then ascribes a value of 1, 0, or –1 to the result based on the whether the slope is positive, zero, or negative.

Largemouth bass concentrations for 12 sites across Florida (including 9 sites in the Everglades) were analyzed for trend significance. The period of record analyzed extended from as early as 1988 to as late as 2000. The data were stratified according to age class since different age classes in any given year reflect different exposure histories. Of a possible 120 categories (i.e., 10 age classes x 12 sites), 66 had sufficient data to test for sign significance (Table 12). The results were split relatively evenly between a significant decline at the 95% confidence level (29 site-cohort combinations) and no trend (34 site-cohort combinations). Significant declines were observed across the state, suggesting a regional effect (e.g., atmospheric deposition), with the most consistent declines across cohorts observed for the two Everglades canal sites, L-67A and L-35B (and East Lake Tohopekaliga. The three sites in Water Conservation 3A near site 3A-15 (located near the so-called “hot spot” of high fish tissue concentrations in WCA-3A) also showed some cohorts with significant declines, although nearly as many site-cohort combinations also showed no change. Only three site-cohort combinations showed a significant increasing trend, and these all were observed at the U3 site in Water Conservation Area 2A. This increase likely reflects a highly localized effect both in time and space, such as peat burning and oxidation that occurred in the Everglades following the intense drought and drydown in May and June 1999 (Pollman et al., 2002). This period of peat oxidation induced a series of short-term but substantial changes in Hg biogeochemistry, including large scale increases in mosquitofish Hg concentrations at site U3, while the response at 3A-15, which remained wet during this period, was more muted (Krabbenhoft and Fink, 2001).

Table 12. Summary of Mann-Kendall Slope Test-of-Sign for trends in mercury concentrations in largemouth bass. Test results are given for individual sites and age cohorts. (-) indicates significant declining trend; (0) indicates no significant trend; and (+) indicates significant increasing trend. Site-cohort combinations with insufficient data are left blank. All results reported at the 95% significance level.

Location\Age Class	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Northern Florida										
Fowlers Bluff		0	0	-	0	0	-	0	0	
Central Florida										
Lake Tohopekaliga		0	-	0	-	0	0			0
East Lake Tohopekaliga		-	-	-	-	-	-	0		
Everglades										
Miami Canal and L-67A		-	-	-	-	-	0	-		
L-35B Canal		0	-	-	-	-	0			
Indian Camp Creek-Rogers		0	0		0	0				
Marsh-15	-	-	0	0	0					
Marsh-GH	0	-	0	-						
Marsh-OM		-	-							
Marsh-U3	+	+	+	0	0					
Big Lostmans Creek	0	0	0	0	0					
North Prong	0	-	0	-	-	0				

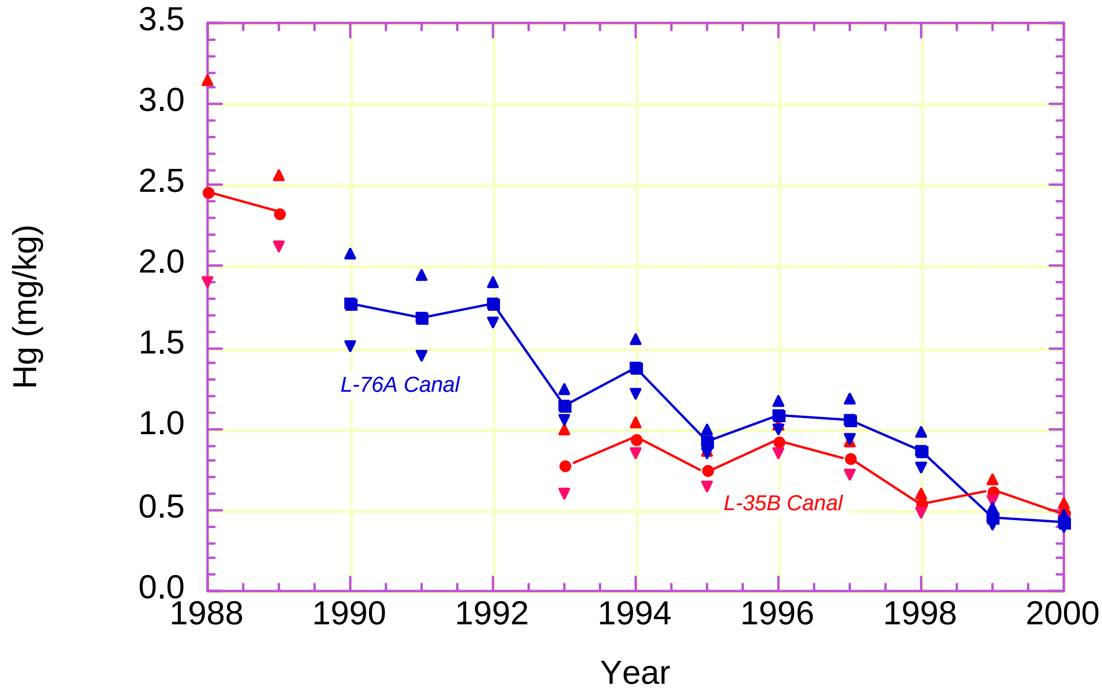

Figure 25. Tissue concentrations of mercury (wet weight) in largemouth bass in the L-67A and L-35B canals in the Florida Everglades. Filled circles show the geometric mean for each year; filled triangles show ± one standard error of the mean.

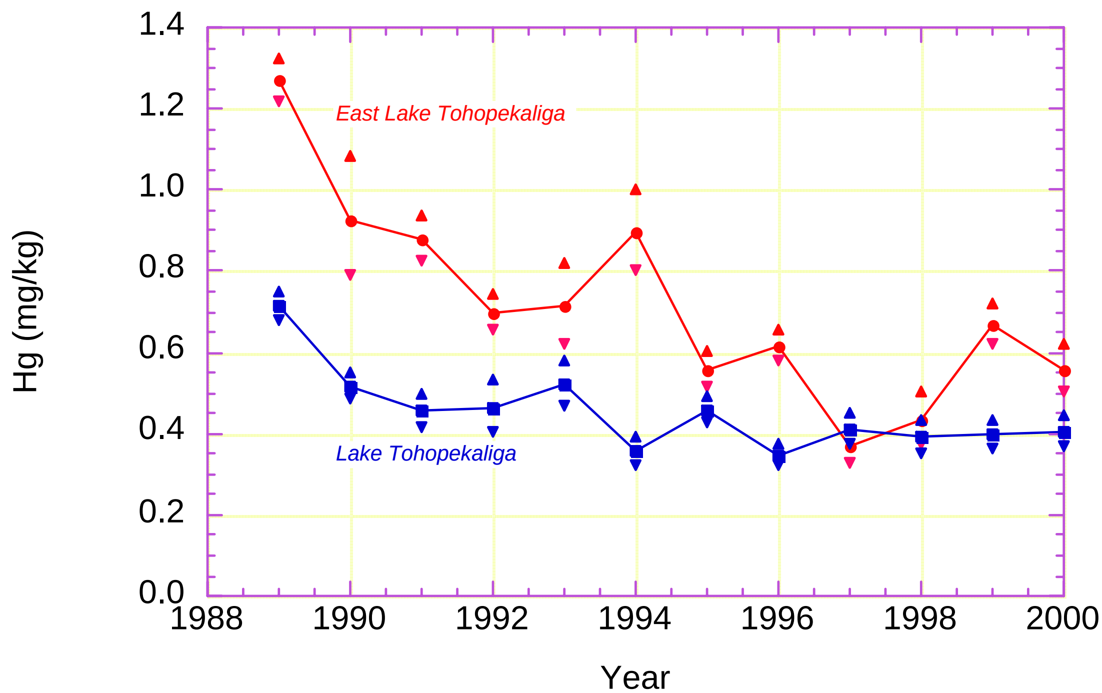

Figure 26. Tissue concentrations of mercury (wet weight) in largemouth bass in East Lake Tohopekaliga and Lake Tohopekaliga located in central Florida. Filled circles show the geometric mean for each year; filled triangles show ± one standard error of the mean.

Great egret chick data from all seven sites studied by Frederick et al. (2001) were tested for trend significance. When Pollman et al. (2002) conducted their trend significance analysis, the time frame spanned by the great egret study extended from 1994 to 2001. Additional data have since been collected, and the full period of record now extends to 2003 (Figure 27). Four sites (Alley, Hidden, JW1, and L67) showed significant downward trends through 2001 based on both the Mann-Kendall test and Sen's median slope analysis. The data from 2002 and 2003 further substantiate the overall robustness of the downward trend. Consistent with the largemouth bass results from the same region, results from colonies located in the mid-Everglades indicate over an 80% decrease in Hg concentrations over the period of 1994-2003.

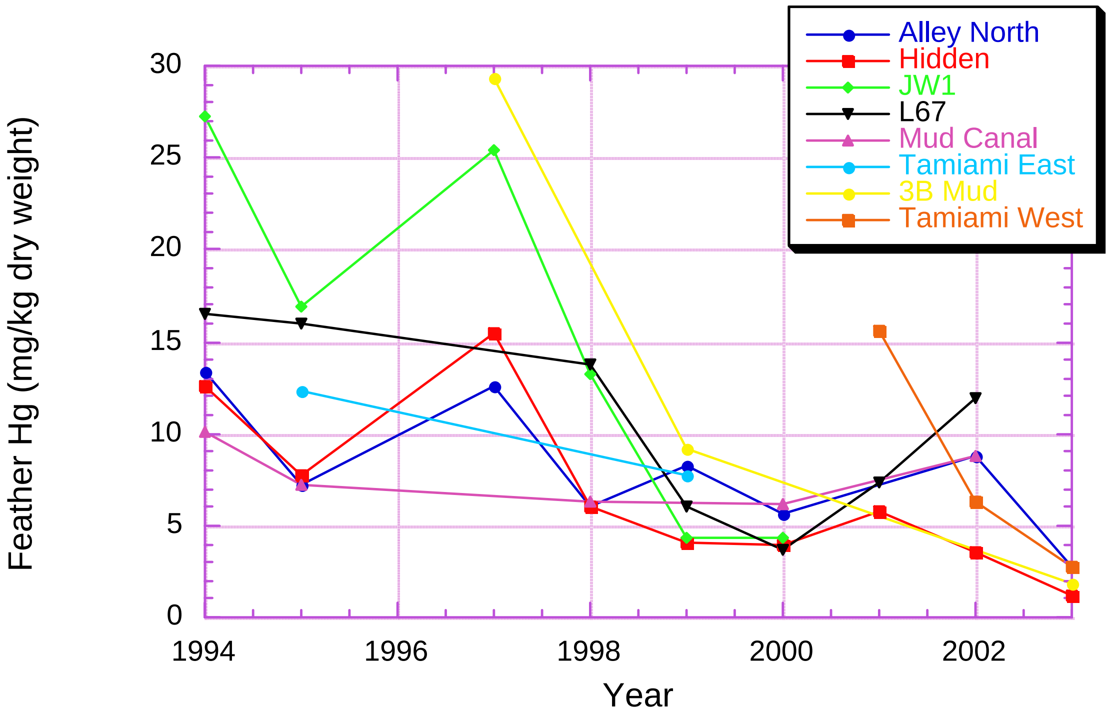

Figure 27. Mercury concentrations in great egret nestlings at various colony locations in the Florida Everglades, 1994 – 2003. Discontinuities in the period of record reflect years when a colony site was abandoned or otherwise not used. Unpublished data courtesy of P. Frederick (2003).

Model Hindcasting

E-MCM was used to predict changes in age 3 largemouth bass mercury concentrations in response to assumed changes in atmospheric loadings of mercury to site 3A-15. A simplified trajectory of changing deposition rates from 1900 through 2000 was developed with several assumptions or constraints imposed:

1. Based on Hg accumulation rates measured in soil cores in WCA-2A (Rood et al., 1995), an increase in modern deposition rates of 7.4-fold (1985 to 1991) over “pre-industrial” (ca. 1900) was assumed. Rood et al. measured an average accumulation rate of 8 $\mu g/m^2$-yr for ca. 1900 compared to 59 $\mu g/m^2$-yr for 1985-1991.
2. We assume that, superimposed upon the long-term background deposition of 8 $\mu g/m^2$-yr inferred from Rood et al., there has been a deposition signal derived from anthropogenic sources (local and larger geographic scale) that tracks the 1970-2000 Hg trend in the municipal solid waste (MSW) inventory compiled by Kearney and Franklin Associates (1991). This inventory shows that Hg in MSW peaked between 1985 and 1990, with a comparatively sharp decline through 1995, followed by relatively stable inventory quantities. As a first order analysis, we also assumed that anthropogenic emissions and associated deposition fluxes increased linearly from 1900 through 1985.
3. After emissions and deposition reached peak levels in 1985, we assumed that deposition declined linearly until 1996, with total mercury deposition reduced to 35 $\mu g/m^2$-yr. Following 1996, we assume that anthropogenic emissions remained constant (although there is evidence of continuing emissions declines). Figure 28 shows the mercury deposition trajectory that resulted from these assumptions.

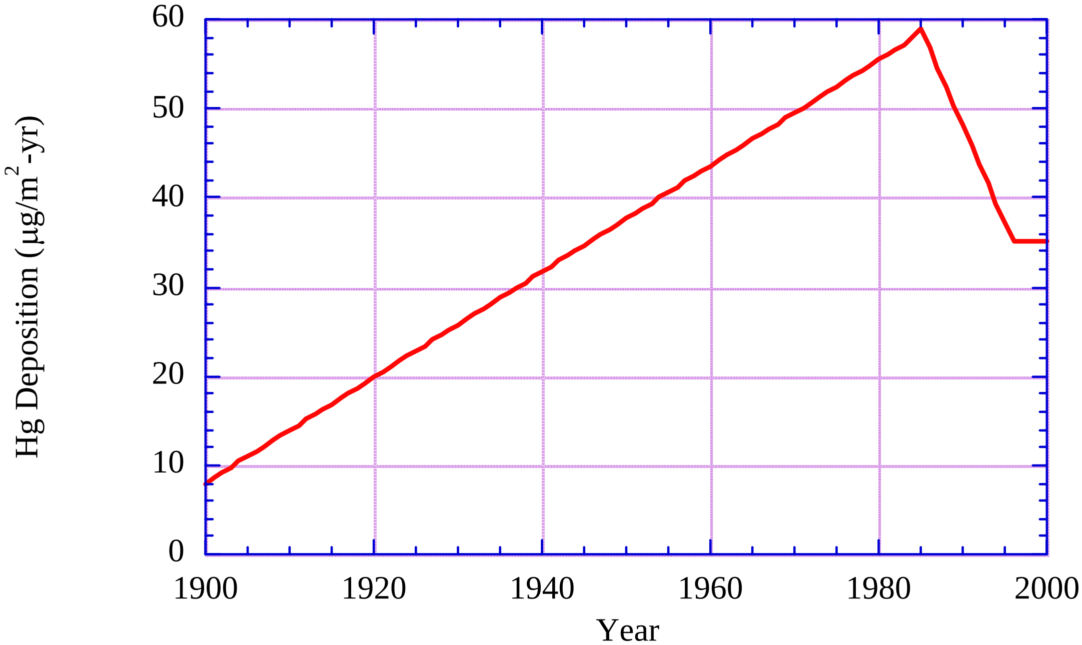

Figure 28. Total (wet + dry deposition) mercury deposition trajectory used in E-MCM model hindcast.

The mercury deposition trajectory was then used as the input forcing function to reconstruct a predicted time series of biotic (largemouth bass) response in south Florida using the E-MCM model. E-MCM had previously been calibrated for a site (site 3A-15) in the Florida Everglades regarded as a "hot spot" for high fish Hg concentrations (Appendix 2). E-MCM was initially run at pre-1900 deposition conditions until steady-state was achieved in all the model compartments (water, sediments, biota). The model then was perturbed by imposing the reconstructed deposition time series, and the predicted biota response compared to the observed trends for ca. 1990-2000. Results are shown in Figure 29. The hindcast simulation predicts a monotonic decline in largemouth bass concentrations on the order of 20% beginning ca. 1989 and continuing through 2000. Although the timing of the response is generally consistent with the observed biota, the magnitude is only about 1/3 the observed decline of ca. 60% (average of all data for south Florida).

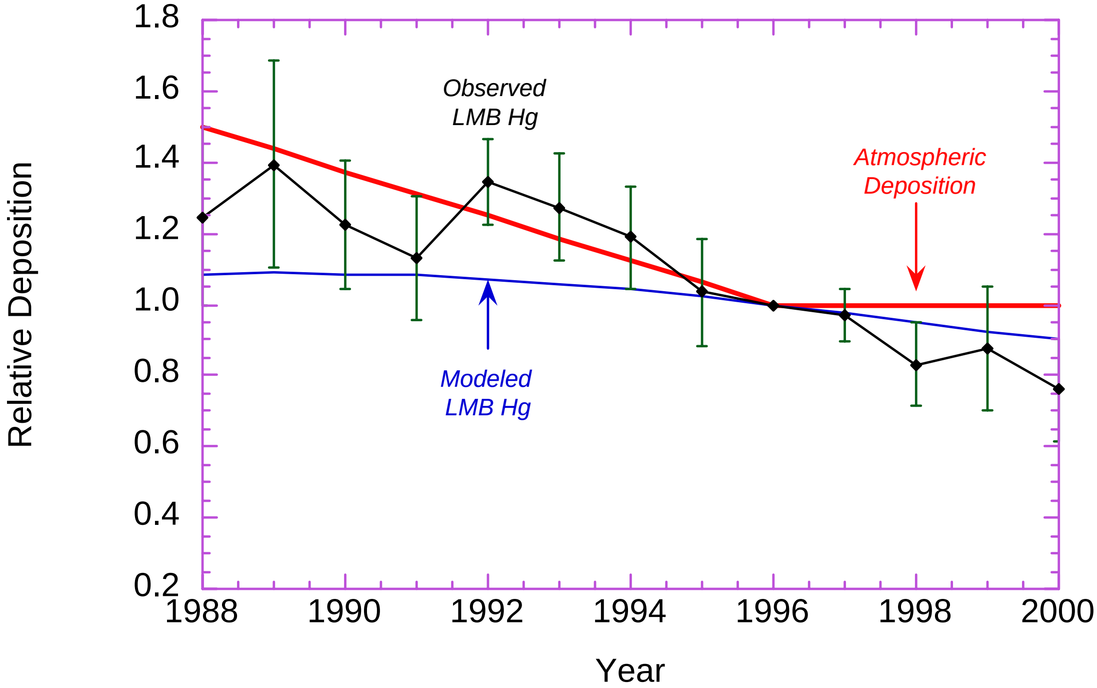

Figure 29. E-MCM simulation hindcast of changes in mercury concentrations in age 3 largemouth bass at 3A-15 in response to assumed changes in atmospheric deposition (see Figure 28). Analysis assumes that the depth of surficial sediments actively exchanging Hg(II) is 3 cm. Shown are normalized (relative to 1996) changes in atmospheric deposition inputs, observed concentrations in largemouth bass, and model results. Error bars are ± 1 standard error of the mean.

Mesocosm experiments currently underway in the Everglades indicate that mercury methylation rates and transfer to the aquatic food chain respond very rapidly in response to new inputs of Hg(II) (D. Krabbenhoft, pers. comm.). These experiments are being conducted using isotopic tracers to elucidate the magnitude and timing of changes in mercury cycling to changes in mercury inputs. Similar results are emerging from the Mercury Experiment To Assess Atmospheric Loading in Canada and the United States (METAALICUS; R. Harris, pers. comm.), which also is using isotopic tracers. E-MCM predicts that the primary pathway for introducing Hg into the foodchain at site 3A-15 is via methylation in the sediments and the benthic foodweb. Thus, the magnitude of the predicted response is governed by the residence time of bioavailable Hg in the sediments, which in turn is governed largely by the mixed depth of actively exchanging surficial sediments. The current assumption is 3 cm and, in light of the recent isotopic tracer experimental results, may prove to be a large overestimate of the size and residence time of the Hg(II) pool available for methylation.

To test the effect the assumed size of the pool of bioavailable Hg in the sediments exerts on the timing and magnitude of biotic response, we ran an additional simulation where the sediment exchange depth was reduced by an order of magnitude to 0.3 cm. The resultant hindcast agrees extremely well with the observed trends in largemouth mercury concentrations, both with respect to timing and the magnitude of change.

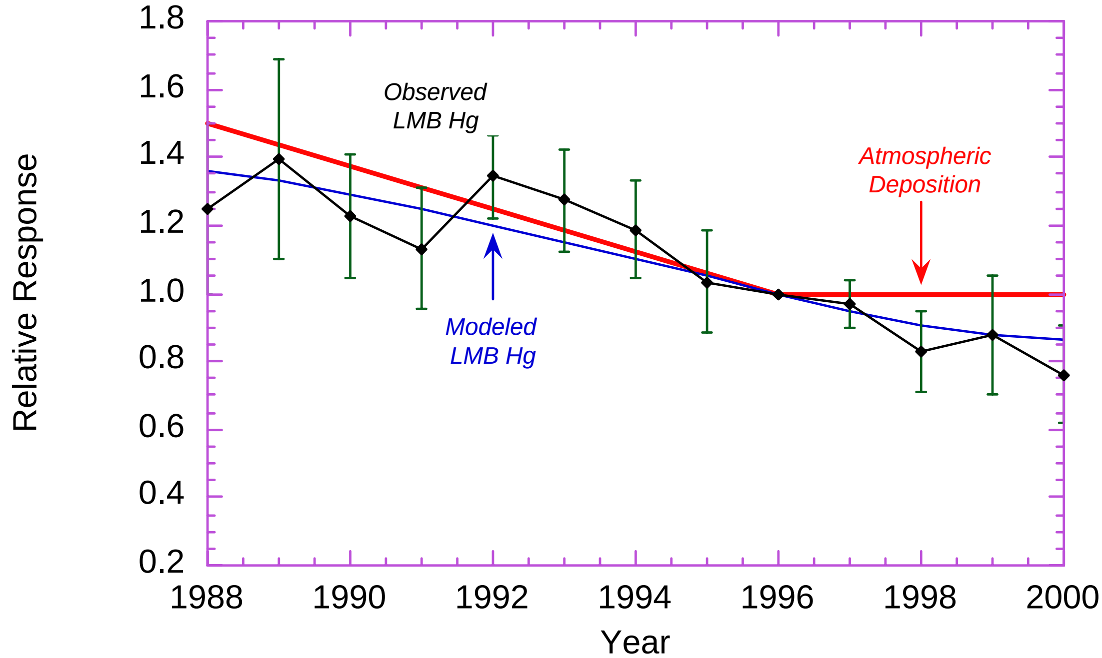

Figure 30. Same as Figure 29, except that the depth of surficial sediments actively exchanging Hg(II) is 0.3 cm.

Discussion and Conclusions

Local emission rates of mercury in south Florida appear to declined by over 90% since peak levels occurring in the late 1980's to early 1990's. This estimate is supported by two completely different approaches towards estimating emissions. Whether these changes in emissions have had a corresponding effect on local deposition rates of mercury in part is a function of the chemical speciation of the emissions. There are two major types of gas phase Hg species present in emissions from combustion sources: elemental Hg or Hg(0), and reactive gaseous mercury (RGM) or Hg(II). Speciation of emissions is critical because it influences greatly how far emitted Hg likely will be transported. Hg(0) reacts in and is deposited from the atmosphere only very slowly, and has a characteristic residence time in the troposphere on the order of 1 year. RGM, on the other hand, is highly reactive, and is scavenged rapidly from the lower troposphere by either wet deposition or by adsorption to settling particles and surfaces. If, for example, there has been a decline in Hg(0) emissions from south Florida, but RGM emissions have remained constant, we would expect little or no change in biota concentrations in the Everglades as a result. On the other hand, if local RGM emissions have declined, but Hg(0) emissions have remained constant, we would expect to see more of a biotic response. By not considering speciation, we risk misinterpreting the true significance of the relationship between local emissions and biotic response. This would be particularly true if Hg(0) emissions greatly predominate. Unfortunately only limited data are available on the speciation of Hg emissions as a function of source, including speciation measurements conducted by Dvonch et al. (1999) from a municipal waste incinerator (8 measurements), a medical waste incinerator (3 measurements) and a cement kiln (3 measurements) in Dade and Broward counties. The fraction of Hg(II) emitted ranged from 25% of the total (cement kiln) to nearly 95% for the medical waste incinerator. The fraction of Hg(II) emitted by the municipal waste incinerator averaged ca. 75%. Since the local emissions inventory for Dade and Broward counties in 1995-96 was dominated by municipal waste and medical waste incineration (ca. 86% of total emissions), it appears likely that Hg(II) emissions were predominant, at least for 1995-96. If these speciation results are similar for historical emission patterns (and there is no reason to expect that Hg(0) emissions were more important), then our approach of examining total emissions and linking the trends to local biota response appears reasonable.

Coupled with changes in local emission rates is evidence that mercury concentrations in wet deposition (annual VWM) in south Florida have declined by about 25% since late 1993. Statistical analysis indicates that the trends are significant, and are due to factors other than seasonal dynamics and changes in precipitation rates. Although the declines in measured VWM concentrations are considerably smaller than the overall decline in local emissions, most of the decline in emissions occurred prior to late 1993 when monitoring of mercury concentrations in wet deposition first began. Indeed, the relatively modest change in VWM concentrations agrees reasonably well with the emissions declines after 1993.

Statistically significant declines in mercury concentrations in both largemouth bass and great egret chicks have been observed for a number of sites in the Everglades. Declines over approximately the past decade for both species are on the order of 80%. Model hindcasting using the E-MCM model calibrated for 3A-15 indicates that changes in atmospheric deposition inferred from sediment core analyses may account for the recent changes in largemouth bass mercury concentrations, both in terms of timing and magnitude of change. For this to be true, however, requires modifying the current model paradigm with respect to the size of the pool of Hg(II) that is readily bioavailable in surficial sediments for methylation (*viz*., reducing the size and residence time of the Hg[II] pool). Such a paradigm shift is consistent with recent isotopic tracers experiments indicating that mercury cycling in aquatic systems responds very rapidly to recent inputs.

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